Physicochemical Characterization of the Loganic Acid–IR, Raman, UV-Vis and Luminescence Spectra Analyzed in Terms of Quantum Chemical DFT Approach

Adam Zajac 1,*, Jacek Michalski 1, Maciej Ptak 2, Lucyna Dymińska 1, Alicja Z. Kucharska 3, Wiktor Zierkiewicz 4, and Jerzy Hanuza 2

Abstract: The molecular structure and vibrational spectra of loganic acid (LA) were calculated using B3LYP density functional theory, the 6–311G(2d,2p) basis set, and the GAUSSIAN 03W program. The solid-phase FTIR and FT-Raman spectra of LA were recorded in the 100–4000 cm⁻¹ range. The assignment of the observed bands to the respective normal modes was proposed on the basis of the PED approach. The stability of the LA molecule was considered using NBO analysis. The electron absorption and luminescence spectra were measured and discussed in terms of the calculated singlet, triplet, HOMO, and LUMO electron energies. The Stokes shift derived from the optical spectra was 20,915 cm⁻¹.

Keywords: loganic acid; molecular structure; IR; Raman spectra; UV-Vis measurements; luminescence; Stokes shift; quantum chemical DFT calculations

1. Introduction

Loganic acid is an iridoid glucoside, an important biologically active component of several fruits such as cornelian cherry, cranberry, bilberry, and honeysuckle berries [1–6]. Iridoids comprise a large group of monoterpenoids with six-membered ring skeletons containing oxygen atoms fused to a cyclopentane ring. They can be extracted from the plants both in the state of cyclopentanopyran monoterpenoid glucoside loganic acid and loganin [7]. The conversion of loganic acid into loganin is catalyzed by loganic acid methyltransferase through the transfer of a methyl group from 5-adenosyl-methionine to the carboxylate of loganic acid [7–9]. Iridoid glycosides also have numerous biological activities [10] such as antifungal [11] and antimicrobial [12]. They are also used in several medicinal applications [13–17].

It should be noted that several plants can be employed in medicinal applications due to the presence of loganic derivatives in their composition. Phytotherapy enables the support of pharmaceutical treatments at all stages of the disease, proposing new types of remedies [16,18–24]. Some of them show antidiabetic and antioxidant effects [16,18] due to the significant amounts of iridoid glucosides and loganic acid. Loganic acid also exhibits activity for treating rheumatoid arthritis [19] and inflammation [20]. This iridoid glucoside shows clear neuroprotective effects [21], defends against diet-induced hypertriglyceridemia and atherosclerosis [22], as well as exhibits antiadipogenic effects [23]. Logenic acid reduces cholesterol in the blood and lipid accumulation in the aortic wall [24].
The significant content of loganic acid and its derivatives in several plants had an effect in the new developed techniques of phytopreparation. Several new extraction methods of the bioactive components of the plants were used for isolation of the iridoids. They allowed us to obtain new medicinal remedies with high concentrations of the iridoids and loganic acid [25–31].

The physicochemical properties and conformation of loganic acid and loganin have rarely been studied and characterized. The $^1$H and $^{13}$C NMR spectra [32,33] and circular dichroism [34] were measured and analyzed. The XRD structures of loganin and its bromo-derivative were reported in papers [35,36]. The present work reported the results of spectroscopic measurements carried out for iridoid loganic acid. IR, Raman, UV-Vis, and luminescence spectra were analyzed in terms of the quantum chemical DFT approach.

In all the cited papers, the preferable technique used for identification of the iridoids in plants was NMR spectroscopy as a fingerprinting tool for interpretation and quality assessment of natural bioactive products. This method allowed the determination of the amount and structure of the iridoids in the plants. Scores of papers used the 1D and 2D NMR methods for the measurements and interpretation of the $^1$H and $^{13}$C spectra. Such an approach was applied in several studies in which some selected natural materials were studied [5,14,28,32,34,35,37–43].

The present work proposed new tools for the identification of loganic acid in plants and their extracts. We reported the results of spectroscopic measurements carried out for iridoid loganic acid. IR, Raman, UV-Vis, and luminescence spectra were analyzed in terms of the quantum chemical DFT approach. The theoretical data were compared with the experimental results obtained from the structural and spectroscopic studies. Such an approach allowed the creation of new tools for the identification of loganic acid, iridoids, and their derivatives present in plants and other natural materials.

2. Results and Discussion

2.1. Molecular Geometry

The optimized molecular structure of loganic acid (LA) with the atoms numbering is shown in Figure 1. The calculated parameters compared to the experimental XRD data reported for loganin [35] are given in Table 1.

![Figure 1. Molecular structure of loganic acid with numbering of atoms.](image-url)
Table 1. Optimized geometrical parameters of loganic acid obtained by DFT calculations compared with the experimental structural data reported for loganin [35].

| Bond Distances | Calc. | Exp. | Bond Angles | Calc. | Exp. |
|----------------|-------|------|-------------|-------|------|
| O1—C16         | 1.442 | 1.426| C11—O1—C19  | 115.5 | 114.7|
| O2—C16         | 1.475 | 1.432| O1—C16—O2   | 108.7 | 109.6|
| O2—C20         | 1.374 | 1.357| C16—O2—C20  | 116.6 | 115.0|
| C20—C17        | 1.354 | 1.333| O2—C20—C17  | 125.1 | 124.4|
| C17—C12        | 1.502 | 1.510| C20—C17—C12 | 122.0 | 123.2|
| C12—C11        | 1.561 | 1.549| C17—C12—C11 | 110.7 | 110.7|
| C11—C16        | 1.515 | 1.509| C17—C12—C15 | 113.9 | 112.3|
| C12—C15        | 1.551 | 1.551| C12—C11—C16 | 113.2 | 113.0|
| C15—C14        | 1.139 | 1.522| C11—C16—O2  | 111.6 | 113.1|
| C14—C13        | 1.562 | 1.522| O1—C19—O4   | 107.7 | 107.5|
| C13—C11        | 1.566 | 1.535| C19—O4—C24  | 113.2 | 111.7|
| C17—C25        | 1.466 | 1.482| O4—C24—C23  | 107.5 | 108.8|
| C25—O9         | 1.243 | 1.197| C24—C23—C22 | 110.0 | 110.7|
| C25—O8         | 1.389 | 1.341| C23—C22—C21 | 111.3 | 111.1|
| C14—O3         | 1.457 | 1.439| C22—C21—C19 | 109.1 | 108.4|
| C13—C18        | 1.537 | 1.528| C12—C15—C14 | 104.8 | 106.3|
| O1—C19         | 1.432 | 1.396| C15—C14—C13 | 105.8 | 103.9|
| O4—C19         | 1.448 | 1.433| C12—C11—C13 | 106.8 | 104.4|
| O4—C24         | 1.473 | 1.422| C16—C11—C13 | 112.6 | 114.2|
| C23—C24        | 1.534 | 1.530| C20—C17—C25 | 115.5 | 120.0|
| C23—C22        | 1.526 | 1.529| C17—C25—O9  | 126.7 | 123.5|
| C22—C21        | 1.522 | 1.515| C17—C25—O8  | 113.0 | 113.4|
| C21—C19        | 1.523 | 1.511| C15—C14—O3  | 113.1 | 111.9|
| C24—C26        | 1.512 | 1.507| C14—C13—C18 | 114.1 | 115.5|
| C26—O10        | 1.453 | 1.418| O4—C24—C26  | 107.8 | 107.0|
| C23—O7         | 1.447 | 1.415| C24—C23—O7  | 108.2 | 112.1|
| C22—O6         | 1.450 | 1.414| C23—C22—O6  | 106.6 | 111.1|
| C21—O5         | 1.449 | 1.419| C22—C21—O5  | 106.3 | 108.7|

Torsion angles

| C20—C17—O1—C19| 115.5 | 114.7|
| C25—O9—C24—C23| 107.5 | 108.8|
| C23—O8—C23—C22| 111.3 | 111.1|
| C14—O3—C22—C21| 109.1 | 108.4|
| C13—C18—C12—C15| 104.8 | 106.3|
| O1—C19—O4—C24| 105.8 | 103.9|
| C12—C11—C13—C18| 106.8 | 104.4|
| C16—C11—C13—C18| 112.6 | 114.2|
| C20—C17—C25—C26| 115.5 | 120.0|
| C17—C25—O9—C19| 126.7 | 123.5|
| C17—C25—O8—C19| 113.0 | 113.4|
| C15—C14—O3—C19| 113.1 | 111.9|
| C14—C13—C18—C26| 114.1 | 115.5|
| O4—C24—C23—O7| 107.8 | 107.0|
| C23—C22—O6—C21| 106.6 | 111.1|
| C22—C21—O5—C20| 106.3 | 108.7|

2.2. Vibrational Spectra

The observed and simulated FTIR and FT-Raman spectra are presented in Figures 2 and 3, respectively. The assignment of the observed bands and calculated wavenumbers to the respective normal modes characterized by the PED procedure is presented in Table 2.
Figure 2. FT-MIR (a) and FT-FIR (b) spectra of the studied loganic acid: (1) experimental spectrum, (2) simulated spectrum.

Figure 3. Raman spectra of the studied loganic acid: (1) observed, (2) simulated.
Table 2. Calculated and experimental vibrational wavenumbers with assignments for loganic acid vibrations.

| No. | Calculated | Experimental | Assignment for Monomer |
|-----|------------|--------------|------------------------|
|     | dimer      | monomer      | IR RS                  |
| 1   | 3582       | 3582         | 3695(12,2)             | ν(OH)-θ(99) |
| 2   | 3579       | 3579         | 3684(11,2)             | ν(OH)-ψ(98) |
| 3   | 3571       | 3571         | 3653(17,1)             | ν(OH)-φ(99) |
| 4   | 3570       | 3570         | 3650(6,0)              | ν(OH)-θ(98) |
| 5   | 3551       | 3551         | 3642(17,1)             | 3400 sh ν(OH-···O)-θ(99) |
| 6   | 3208       | 3208         | 3613(28,2)             | 3334 vs,b ν(OH-···O)-θ(98) (A group) |
| 7   | 3098       | 3098         | 3081(0,2)              | ν(CH)-φ(99) |
| 8   | 3091       | 3091         | 2995(7,2)              | 3086 w ν(CH)-Φ(99) |
| 9   | 3089       | 3089         | 2993(7,2)              | νas(CH3)-φ(99) |
| 10  | 3061       | 3061         | 2998(3,2)              | νas(CH2)-ψ(89) |
| 11  | 3026       | 3026         | 2974(10,1)             | νas(CH3)-φ(97) |
| 12  | 3025       | 3025         | 2964(5,1)              | ν(CH)-Φ(94) |
| 13  | 3014, 3014, 3008 | 2946(10,3) | νas(CH2)-θ(93) |
| 14  | 2999       | 2999         | 2936(2,1)              | ν(CH)-Φ(92) |
| 15  | 2997       | 2997         | 2934(10,2)             | ν(CH)-θ(74) |
| 16  | 2992       | 2992         | 2925(6,2)              | νas(CH2)-φ(82) |
| 17  | 2987       | 2987         | 2922(4,3)              | ν(CH)-θ(85) |
| 18  | 2980       | 2980         | 2917(7,3)              | ν(CH)-ψ(75) |
| 19  | 2971       | 2971         | 2889(28,1)             | νas(CH2)-ψ(93) |
| 20  | 2967       | 2967         | 2885(8,1)              | 2963 s 2963 sh ν(CH)-θ(98) |
| 21  | 2958       | 2958         | 2876(2,3)              | ν(CH)-θ(90) |
| 22  | 2956       | 2956         | 2868(2,3)              | 2928 s 2936 vs νas(CH2)-θ(91) |
| 23  | 2867       | 2833(16,3)   | 2882 s 2884 s ν(CH)-θ(96) |
| 24  | 2726       | 2822(2,0)    | vs(CH2)-ψ(89)         |
| 25  | 1644       | 1638         | 1747(92,2)             | 1677 s 1682 s ν(C=O)-Φ(A group) (69) |
| 26  | 1615       | 1605         | 1623(100,8)            | 1632 s 1634 vs ν(Φ) (45) + ν(C=C=O) (A group) (17) |
| 27  | 1519       | 1519         | 1486(2,1)              | 1517 vv 1526 vv δas(CH2)-θ(75) + δ(COH)-θ(11) |
| 28  | 1517       | 1517         | 1481(1,1)              | δas(CH2)-ψ(77) |
| 29  | 1511       | 1511         | 1477(2,1)              | 1490 sh δas(CH3)-φ(87) |
| 30  | 1503       | 1503         | 1468(2,1)              | 1481 sh δas(CH3)-φ(90) |
| 31  | 1460       | 1442(1,0)    | 1458 w 1459 m δ(CH2OH)-θ(72) |
| 32  | 1449       | 1449         | 1415(2,1)              | 1454 sh δ(COH)-θ(42) + δ(CCH)-θ(31) |
| 33  | 1439       | 1404(9,0)    | δs(CH3)-φ(56) + δ(CCH)-ψ(24) |
| No. | Calculated | Experimental | Assignment for Monomer |
|-----|------------|--------------|-----------------------|
| 34  | 1435       | 1434         | 1405(1,0) $\delta$(COH)-$\theta$(53) + $\delta$(CCH)-$\theta$(34) |
| 35  | 1425       | 1425         | 1404(1,1) $\nu$(\(\theta\)) (49) + $\nu$(COC) (25) |
| 36  | 1416       | 1416         | 1396(1,1) 1416 w 1416 sh $\nu$(\(\theta\)) (43) + $\nu$(COC) (30) |
| 37  | 1410       | 1410         | 1394(7,0) 1412 sh 1408 sh $\nu$(\(\varphi\)) (59) |
| 38  | 1403       | 1403         | 1385(1,0) $\nu$(\(\varphi\)) (49) + $\delta$(CCH)-$\varphi$(34) |
| 39  | 1403       | 1402         | 1377(6,0) 1405 sh $\nu$(\(\theta\)) (58) + $\delta$(CCH)-$\vartheta$(24) |
| 40  | 1397       | 1397         | 1375(0,1) $\nu$(\(\Phi\)) (93) |
| 41  | 1382       | 1382         | 1368(5,1) 1384 sh $\nu$(\(\varphi\)) (84) |
| 42  | 1376       | 1376         | 1363(9,1) 1378 sh $\nu$(\(\varphi\)) (78) |
| 43  | 1371       | 1371         | 1349(9,0) 1374 w 1372 m $\nu$(\(\varphi\)) (38) + $\delta$(CCH)-$\varphi$(29) |
| 44  | 1369       | 1369         | 1347(13,0) 1363 sh $\nu$(\(\theta\)) (54) + $\delta$(CCH)-$\theta$(27) |
| 45  | 1355       | 1355         | 1341(2,0) $\nu$(COC) (27) + $\delta$(CCH)-$\Phi$(25) |
| 46  | 1353       | 1353         | 1337(4,1) $\nu$(COC) (29) + $\nu$(\(\Phi\)) (25) |
| 47  | 1351       | 1351         | 1329(3,1) $\nu$(\(\Phi\)) (72) |
| 48  | 1345       | 1345         | 1325(5,0) 1347 w $\nu$(\(\theta\)) (50) + $\delta$(COH)-$\theta$(25) |
| 49  | 1337       | 1337         | 1324(16,0) 1340 sh $\nu$(\(\theta\)) (55) + $\nu$(COC) (32) |
| 50  | 1330       | 1330         | 1304(14,0) 1331 w $\nu$(\(\varphi\)) (44) + $\delta$(CCH)-$\varphi$(23) |
| 51  | 1323       | 1323         | 1299(2,0) $\nu$(\(\theta\)) (60) + $\delta$(COH)-$\theta$(21) |
| 52  | 1308       | 1308         | 1284(6,0) 1310 sh $\nu$(\(\varphi\)) (41) + $\delta$(CCH)-$\varphi$(35) |
| 53  | 1301       | 1295         | 1269(1,1) $\nu$(\(\Phi\)) (47) + $\delta$(CCH)-$\Phi$(22) |
| 54  | 1295       | 1294         | 1264(2,0) 1295 sh $\nu$(\(\varphi\)) (35) + $\delta$(CCH)-$\varphi$(24) |
| 55  | 1293       | 1292         | 1254(11,0) $\nu$(C-CH$_3$)-$\theta$(54) + $\delta$(COH)-$\theta$(19) |
| 56  | 1283       | 1283         | 1241(5,0) 1276 m 1276 sh $\delta$(CH$_2$)-$\theta$(64) + $\delta$(COH)-$\theta$(34) |
| 57  | 1261       | 1261         | 1238(12,1) 1260 sh 1264 w $\delta$(COH)-$\theta$(55) |
| 58  | 1239       | 1239         | 1223(6,0) 1254 sh $\nu$(\(\varphi\))-(49) + $\delta$(CCH)-$\varphi$(29) |
| 59  | 1238       | 1238         | 1221(8,0) $\delta$(COH)-$\varphi$(44) + $\delta$(CCH)-$\varphi$(35) |
| 60  | 1230       | 1230         | 1219(12,1) $\delta$(CCH)-$\theta$(71) + $\nu$(\(\varphi\))-(24) |
| 61  | 1222       | 1222         | 1201(15,0) $\nu$(\(\varphi\)) (35) + $\delta$(CCH)-$\Phi$(34) + $\nu$(\(\Phi\)) (29) |
| 62  | 1220       | 1220         | 1180(31,0) $\nu$(\(\varphi\)) (53) + $\delta$(CCH)-$\theta$(27) + $\delta$(COH)-$\theta$(10) |
| 63  | 1196       | 1196         | 1177(33,1) 1202 sh 1200 w $\nu$(\(\varphi\)) (47) + $\delta$(C-COOH)-$\Phi$(38) |
| 64  | 1191       | 1191         | 1163(22,0) 1182 m 1185 sh $\delta$(C-COOH)-$\Phi$(44) + $\nu$(\(\Phi\)) (41) |
| No. | Calculated | Experimental | Assignment for Monomer |
|-----|------------|--------------|------------------------|
| 65  | 1163       | 1162         | 1148(9,1)              |
| 66  | 1149       | 1148         | 1134(7,2)              |
| 67  | 1138       | 1138         | 1130(4,0)              |
| 68  | 1136       | 1136         | 1117(11,0)             |
| 69  | 1121       | 1121         | 1108(10,1)             |
| 70  | 1101       | 1101         | 1097(20,1)             |
| 71  | 1088       | 1088         | 1091(1,1)              |
| 72  | 1080       | 1078         | 1083(10,1)             |
| 73  | 1077       | 1075         | 1077(51,3)             |
| 74  | 1072       | 1069         | 1068(92,0)             |
| 75  | 1066       | 1064         | 1058(9,1)              |
| 76  | 1059       | 1058         | 1049(37,1)             |
| 77  | 1051       | 1051         | 1046(20,1)             |
| 78  | 1043       | 1042         | 1040(56,0)             |
| 79  | 1035       | 1034         | 1039(54,1)             |
| 80  | 1026       | 1026         | 1029(50,0)             |
| 81  | 1021       | 1019         | 1018(49,0)             |
| 82  | 1015       | 999(39,0)    | 1016 sh                |
| 83  | 1006       | 1006         | 990(28,0)              |
| 84  | 997        | 997          | 979(6,0)               |
| 85  | 994        | 993          | 978(11,1)              |
| 86  | 978        | 977          | 977(36,1)              |
| 87  | 971        | 971          | 971(11,1)              |
| 88  | 959        | 958          | 952(2,0)               |
| 89  | 917        | 916          | 918(11,0)              |
| 90  | 895        | 894          | 897(3,1)               |
| 91  | 876        | 876          | 886(25,1)              |
| 92  | 846        | 846          | 843(4,2)               |
| 93  | 812        | 811          | 826(36,1)              |
| 94  | 789        | 789          | 784(2,3)               |
| 95  | 757        | 756          | 772(12,1)              |
| 96  | 741        | 729          | 730(1,5)               |

Table 2. Cont.
| No. | Calculated | Experimental | Assignment for Monomer |
|-----|------------|--------------|------------------------|
| 97  | 704        | 701          | 700(2,1) δ(C–O–C) (49) + τ(Φ-COOH) (43) |
| 98  | 682        | 679          | 669(22,2) δ(C–O–C) (78) + ρ(Φ-COOH) (21) |
| 99  | 650        | 650          | 660(1,0) τ(Φ-COOH) (86) + γ(ψ) (13) |
| 100 | 615        | 615          | 614(10,0) τ(Φ-COOH) (61) + γ(ψ) (33) |
| 101 | 609        | 609          | 606(11,1) τ(Φ-COOH) (61) + γ(ψ) (33) |
| 102 | 603(5,0)   | 601          | γ(C–O–C) (51) + τ(Φ-COOH) (36) |
| 103 | 590        | 590          | 598(8,2) γ(θ) (47) + γ(θ-OH) (44) |
| 104 | 583        | 583          | 587(6,1) γ(ψ) (58) + τ(ϕ-CH3) (43) |
| 105 | 564        | 560          | 560 τ(θ-OH) (57) + γ(θ-O-Φ) (93) |
| 106 | 551        | 538          | 540 τ(θ-OH) (61) + γ(θ) (20) |
| 107 | 532        | 526          | 523(2,2) τ(θ-OH) (39) + τ(θ-CH2OH) (37) + γ(θ) (20) |
| 108 | 517        | 505          | 497(2,1) τ(θ-OH) (39) + τ(θ-CH2OH) (37) + γ(θ) (20) |
| 109 | 476        | 471          | 472(3,1) γ(ψ) (56) + τ(θ-OH) (37) |
| 110 | 465        | 462          | 451(2,2) τ(θ-OH) (61) + γ(θ) (20) |
| 111 | 452        | 448          | 442(1,1) τ(θ-OH) (54) + γ(θ) (20) |
| 112 | 441        | 441          | 428(5,2) τ(θ-OH) (62) + γ(θ) (20) |
| 113 | 433        | 433          | 417(20,3) τ(θ) (47) + γ(θ-O-Φ) (43) |
| 114 | 425        | 424          | 409(17,1) γ(θ) (51) + τ(θ-OH) (43) |
| 115 | 417        | 416          | 389(4,1) 419 w τ(θ-OH) (34) + γ(Φ) (32) + τ(θ) (31) |
| 116 | 400        | 399          | 380(35,4) τ(θ-OH)(31) + τ(θ-CH2OH) (30) + τ(θ-CH2OH) (29) |
| 117 | 386        | 382          | 371(1,1) τ(θ-CH2OH) (33) + τ(θ-OH) (32) + τ(θ-O-Φ) (32) |
| 118 | 370        | 368          | 337(6,5) 362 sh γ(θ) (64) + τ(θ-CH2OH) (32) |
| 119 | 336        | 335          | 312(1,2) 333 w ω(θ-Ο-Φ-ψ) (94) |
| 120 | 329        | 319          | 307(2,1) 328 w τ(HO-θ-OH) (48) + τ(HO-ψ-Φ) (45) |
| 121 | 310        | 302          | 291(1,3) τ(HO-ψ-CH3) (94) |
| 122 | 298        | 292          | 287(1,1) τ(HO-ψ-CH3) (68) + ρ(θ-OH) (37) |
| 123 | 287        | 287          | 281(2,1) ρ(ϕ-CH3) (38) + ρ(θ-OH) (29) + ρ(ϕ-OH) (29) |
| 124 | 284        | 283          | 263(21,0) τ(ψ-OH) (95) |
| 125 | 270        | 268          | 244(3,1) 266 w τ(HO-θ-OH) (53) + τ(θ) (41) |
Table 2. Cont.

| No.   | Calculated | Experimental | Assignment for Monomer |
|-------|------------|--------------|------------------------|
| 126   | 263        | 251          | τ(θ-CH₂OH) (57) + τ(HO-θ-OH) (41) |
| 127   | 244        | 244          | τ(ϕ) (47) + τ(ϕ-COOH) (45) |
| 128   | 234        | 233          | τ(ϕ-CH₃) (96) |
| 129   | 230        | 230          | τ(θ-CH₂OH) (53) + τ(HO-θ-OH) (46) |
| 130   | 221        | 218          | τ(ϕ-COOH) (66) + τ(φ) (31) |
| 131   | 215        | 214          | τ(HO-θ-OH) (41) |
| 132   | 184        | 184          | τ(θ-CH₂OH) (57) |
| 133   | 171        | 170          | τ(θ-CH₂OH) (57) |
| 134   | 161        | 160          | τ(θ-CH₂OH) (57) + τ(HO-θ-OH) (41) |
| 135   | 132,126    | 130          | τ(θ-CH₂OH) (49) + τ(HO-θ-OH) (43) |
| 136   | 115        | 116          | τ(HO-θ-OH) (34) + τ(θ-CH₂OH) (36) |
| 137   | 107        | 101          | τ(θ) (56) + τ(θ-CH₂OH) (29) + τ(θ-O-Φ) (11) |
| 138   | 102,97     | 89           | τ(θ-COH) (49) + τ(θ-CH₂OH) (45) |
| 139   | 78         | 80           | τ(Φ-COOH) (58) + τ(Φ) (44) |
| 140   | 73         | 72           | τ(Φ) (54) + ρ(C-COOH)-Φ (33) |
| 141   | 65         | 64           | τ(θ) (48) + ρ(COH)-θ (40) |
| 142   | 39         | 38           | τ(θ-Φ) (57) + ρ(COH)-ϕ (36) |
| 143   | 33         | 30           | τ(θ-Φ-ϕ) (70) + τ(COH)-ϕ (19) |
| 144   | 24         | 22           | τ(θ) (79) |

Abbreviations used: s—strong; m—medium; w—weak; v—very; sh—shoulder; v—in-plane stretching vibrations (s—symmetric; as—asymmetric); δ—in-plane bending vibrations; γ—out-of-plane bending vibrations; τ—torsional; ρ—rocking; ω—wagging vibrations. θ—carbohydrate ring; Φ—pyran ring of the cycloptentane[cyran (iridoid) system; ϕ—cyclopentane ring of the cyclopenta[cyran system; θ-O-Φ and C-O-C—glycosidic bridge bond; COO—carboxyl group. Used scaling factor: for monomer fsc = 0.96 (2500–3700 cm⁻¹), fsc = 0.98 (0–2500 cm⁻¹); for dimer fsc = 0.98 (0–3700 cm⁻¹).

2.2.1. Vibrations of the Cyclopentane[cyran System (Φ, ϕ and Coupled Φϕ)

The cyclopentane[cyran double-ring (Φϕ) system is built of 9 atoms, giving rise to 21 vibrational modes. Ten of them originate from 10 stretching vibrations but the remaining modes correspond to bending and torsion vibrations. Due to the dimeric structure of loganic acid, the number of these modes should double. Therefore, the assignment of the bands presented in Table 2 shows that these modes are characterized by pairs of calculated wavenumbers. They are observed in the range of 800–1650 cm⁻¹ in which both IR and Raman spectra contain a very wide spectral pattern that also follows from the existence of one double C=C bond in this system. A total of 21 modes described in Table 2 as vibrations of the cyclopentane[cyran double-ring system could be subdivided into the vibrations in which the pyran Φring is involved only, in which the cyclopentane ϕring participates only and the modes of a mixed nature, and in which the coupled Φϕdouble ring system vibrates in the concerted motion. For example, the following bands observed at 1416,
1331, and 1182–1185 cm$^{-1}$ should be assigned to the nearly pure stretching vibrations of the pyran ring, those at about 900–930 and 840 cm$^{-1}$ to the $\delta(\Phi)$ vibrations, those at 772–780 cm$^{-1}$ to the $\gamma(\Phi)$ vibrations, and those at 80–100 cm$^{-1}$ to the $\tau(\Phi)$ vibrations. Similarly, the bands observed at about 1408, 1320, 1270, and 1147 cm$^{-1}$ originate from the predominant contribution of the $\nu(\phi)$ vibrations, those at about 995–999 and 864–865 cm$^{-1}$ to the $\delta(\phi)$ vibrations, and those at about 250 cm$^{-1}$ to the $\tau(\phi)$ vibrations. The concerted vibrations in which $\Phi$ and $\phi$ rings commonly participate are observed at about 1270–1335, 1180–1270, and 1147 cm$^{-1}$ originating from the stretching motions, at about 968, 894–897, and 835–837 cm$^{-1}$ from in-plane bending $\delta(\Phi\phi)$ modes, at about 750–800, 540–600, and 505 cm$^{-1}$ from the out-of-plane bending $\gamma(\Phi\phi)$ modes, and at about 180–270 and 50–100 cm$^{-1}$ from the torsional $\tau(\Phi\phi)$ motions. The appearance and the number of these vibrations confirm that the whole cyclopentane[c]pyran ($\Phi\phi$) system appears in a sofa conformation, similar to that proposed for loganin [35] and the molecular structure derived from DFT calculations carried out in this paper (Figure 1).

2.2.2. Vibrations of the Pyran Ring

The vibrations of the pyran ring are well defined in the literature [44,45]. The wavenumbers calculated here and their assignment to the respective normal modes agree with these data. The following vibrations have been identified in the present work for this component of loganic acid: $\nu(\theta)$: 1440–1450, 1372–1374, 1347, 1200–1240, 1150–1153, 1080–1100, and 1028–1029 cm$^{-1}$; $\delta(\theta)$ at about 979 and 900–930 cm$^{-1}$; $\gamma(\theta)$: 419–421 cm$^{-1}$; and $\tau(\theta)$ at about 266 and 140–150 cm$^{-1}$. The vibrations of the C-C-H systems of the pyran ring are observed in the following ranges: $\nu(CH)$: 3016–3087 cm$^{-1}$; $\delta(CH)$: 1100–1480 cm$^{-1}$; $\rho(CH)$: 570–700 cm$^{-1}$; and $\gamma(\phi)$: 450–490 cm$^{-1}$. Other vibrations of the pyran system correspond to the CH$_2$ substituent. Its vibrations appear in the ranges: $\nu_{as}(CH_2)$: 3050–3080 cm$^{-1}$; $\nu_{s}(CH_2)$: 2780–3035 cm$^{-1}$; $\delta(CH_2)$: 1375–1435 cm$^{-1}$; $\omega(CH_2)$: 1120–1365 cm$^{-1}$; $\tau(CH_2)$: 1090–1200 cm$^{-1}$; and $\rho(CH_2)$: 720–825 cm$^{-1}$.

2.2.3. Carboxylic Group Vibrations

Due to the presence of strong intermolecular hydrogen bonds, carboxylic acids usually exist as dimers. Such an interaction also appears in the case of loganic acid. The recorded IR and Raman spectra exhibit several patterns of bands characteristic for the dimeric arrangement of two carboxylic groups. As an effect of the hydrogen bonds presence, the broad spectral pattern at 2000–3600 cm$^{-1}$ is observed. It results from the overlapping of the bands originating from the vibrations of several O-H groups bonded to the cyclopentane[c]pyran system and pyran rings. The maximum of this band appears at 3334 cm$^{-1}$ (calculated at 3273 cm$^{-1}$). The shape of this broad band can clearly be distinguished from the sharp bands corresponding to the CH, CH$_2$, and CH$_3$ group vibrations observed in the range of 2700–3100 cm$^{-1}$.

The wavenumber of the bands corresponding to the stretching $\nu(C=O)$ vibrations reflects the involvement of the carboxylic CO groups in the HB intermolecular interactions. The vibration wavenumber of this group calculated for the monomeric form of loganic acid is at 1783 cm$^{-1}$, whereas, for the dimer, they are at 1678 and 1671 cm$^{-1}$ for the IR and Raman spectrum, respectively (Table 2). As this band is observed in these spectra at 1677 and 1682 cm$^{-1}$, this confirms the appearance of loganic acid in the dimeric form.

The DFT calculations carried out for the dimeric loganic acid also allowed one to assign other vibrations of its carboxylic group. The C-O stretching and in-plane C-OH bending are expected in the wide range of 1150–1450 cm$^{-1}$ depending on whether the acid is monomeric or dimeric [46]. These vibrations are observed at the following wavenumbers: $\nu(OH)$: 3334 cm$^{-1}$; $\nu(C-COOH)$: 1200–1202 cm$^{-1}$; $\gamma(OH)$: 937 and 752–759 cm$^{-1}$; $\tau(C-COOH)$: 667, 631–634, and 614–623 cm$^{-1}$; $\rho(C-COOH)$: 532–533; and $\tau(C-COOH)$: about 227 cm$^{-1}$.

2.2.4. Vibrations of the C–O–C, i.e., $\theta$-O-$\Phi$Bridged Bond

The vibrations of the C–O–C system are described by four normal modes: asymmetric $\nu_{as}(COC)$ stretching, symmetric $\nu_{s}(COC)$ stretching, in-plane bending $\delta(COC)$, and out-of-
plane bending \( \gamma \) (COC) vibrations. The respective wavenumbers observed for loganic acid are located in the following ranges: \( \nu_{as} \): 1150–1153 cm\(^{-1} \); \( \nu_{s} \): 978–979 and 937–960 cm\(^{-1} \); \( \delta \): 673–704 cm\(^{-1} \); \( \gamma \): 573–601 cm\(^{-1} \); \( \omega \): 333 cm\(^{-1} \); and \( \tau \): 175 and 115 cm\(^{-1} \). Apart from these bands, several other modes exhibit participation of the C–O–C vibrations. Such a character appears for the bands observed at the wavenumbers: 1416–1425, 1353–1355, 1340, 1138, 530–533, 433, and 382–386 cm\(^{-1} \).

2.2.5. Vibrations of the CH, CH\(_2\), and CH\(_3\) Chromophores

Apart from the above-discussed bands, several other vibrations are observed in the analyzed spectra. They correspond to the vibrations of the CH, CH\(_2\), and CH\(_3\) substituents of the ring components of loganic acid. They appear in the well-recognized ranges reported in the literature [45]. They are shown in Table 2.

2.3. UV-Vis and Luminescence Spectra-Electron States and NBO Analysis

Natural bond orbital analysis is an efficient method reflecting the intra- and intermolecular interactions in the studied compound, as well as the effect of charge transfer in a molecular system. Table 3 lists the atomic charges calculated for loganic acid.

Table 3. Atomic charges of loganic acid derived from the NBO analysis.

| Atomic Numbering | Mulliken Atomic Charges | NBO Atomic Charge | Atomic Numbering | Mulliken Atomic Charges | NBO Atomic Charge |
|------------------|-------------------------|-------------------|------------------|-------------------------|-------------------|
| O1               | –0.548                  | –0.591            | C26              | 0.251                   | –0.015            |
| O2               | –0.470                  | –0.549            | H27              | 0.037                   | 0.223             |
| O3               | –0.503                  | –0.749            | H28              | 0.058                   | 0.225             |
| O4               | –0.548                  | –0.610            | H29              | 0.049                   | 0.200             |
| O5               | –0.522                  | –0.736            | H30              | 0.035                   | 0.161             |
| O6               | –0.544                  | –0.755            | H31              | 0.049                   | 0.202             |
| O7               | –0.545                  | –0.748            | H32              | 0.047                   | 0.211             |
| O8               | –0.430                  | –0.711            | H33              | 0.063                   | 0.191             |
| O9               | –0.430                  | –0.633            | H34              | 0.061                   | 0.197             |
| O10              | –0.500                  | –0.735            | H35              | 0.063                   | 0.208             |
| C11              | –0.083                  | –0.245            | H36              | 0.057                   | 0.192             |
| C12              | –0.085                  | –0.224            | H37              | 0.002                   | 0.144             |
| C13              | –0.127                  | –0.220            | H38              | 0.073                   | 0.201             |
| C14              | 0.278                   | 0.166             | H39              | 0.057                   | 0.196             |
| C15              | –0.067                  | –0.403            | H40              | 0.235                   | 0.455             |
| C16              | 0.591                   | 0.456             | H41              | 0.022                   | 0.157             |
| C17              | –0.201                  | –0.255            | H42              | 0.036                   | 0.169             |
| C18              | –0.119                  | –0.563            | H43              | 0.041                   | 0.179             |
| C19              | 0.473                   | 0.437             | H44              | 0.033                   | 0.160             |
| C20              | 0.275                   | 0.259             | H45              | 0.042                   | 0.176             |
| C21              | 0.246                   | 0.095             | H46              | 0.247                   | 0.454             |
| C22              | 0.246                   | 0.107             | H47              | 0.256                   | 0.470             |
| C23              | 0.275                   | 0.115             | H48              | 0.263                   | 0.470             |
| C24              | 0.180                   | 0.105             | H49              | 0.249                   | 0.483             |
| C25              | 0.594                   | 0.822             | H50              | 0.243                   | 0.455             |
Analyzing the values of the calculated atomic charges shown in Table 3, the following conclusions can be drawn:

1. The polar character of the C–O–C bridge follows from the positive 0.437 and 0.456 values of the charges on the carbon C8 and C9 atoms and the negative value of −0.591 on the oxygen atom.
2. Oxygen atoms inside the θ ring and Φ ring exhibit the charges −0.61 and −0.59, respectively, i.e., they have similar character.
3. All the hydroxyl groups appearing in the loganic molecule exhibit similar electron properties—the atomic charges of the oxygen atoms take the values from −0.735 to −0.755.
4. The charges of the carbon atoms differ depending on the place inside the ring and substituent bonded to this atom. The carbon atoms of the pyran θ ring have positive charge (0.095, 0.107, 0.115, 0.105, and 0.437)—the greatest value corresponds to the atom bonded to the bridging oxygen. Another situation appears in the coupled cyclopentane-pyran Φ system. Its carbon atoms change their charge from positive values, 0.456, 0.259, and 0.202, to negative, −0.220, −0.224, −0.245, −0.255, and −0.403. The greatest value appears for the carbon joining the bridging oxygen atom and the smallest value belongs to the C15 atom in the Φ ring.
5. The peculiar situation is observed for the carboxyl group where the C25 atom has charge 0.822, the O9 oxygen atom of the C=O group has charge −0.633, the O8 oxygen atom of the OH group has charge −0.711, and the H49 hydrogen atom has charge 0.483 (see atomic numbering in Figure 1).

The above-specified distribution of the atomic charges should strongly influence the electron transitions observed in the UV-Vis and luminescence spectra, and it should especially be reflected in the HOMO–LUMO transitions. The picture of this transition is shown in Figure 4.

![HOMO-LUMO plots of loganic acid.](image)

Figure 4. HOMO–LUMO plots of loganic acid.

Natural bond analysis is an effective method for studying intra- and inter-molecular bonds, the interaction between bonds, and charge transfer in the molecular system. NBO also informs about interactions between filled donor and empty acceptor orbitals. The results of the theoretical calculation of the HOMO–LUMO energies for the studied compound are shown in Table 4. The calculated values of the chemical hardness, softness, chemical potential, electronegativity, and electrophilicity index of the studied molecule are 2.84, 0.18, −3.78, 3.78, and 2.52, respectively, and are also presented in Table 4. Generally, considering the chemical hardness, a large HOMO–LUMO gap indicates a hard molecule, whereas a small HOMO–LUMO gap represents a soft molecule. The data presented in Table 4 clearly show that the structure of loganic acid is very hard as its HOMO–LUMO energy gap is very large and, simultaneously, its softness is very small. This significant energy gap fits well...
the large experimental energy transition derived from the measurements of the electron absorption spectra (Figure 5). Besides, the hard structure of loganic acid follows from its dimeric organization and stiffing by hydrogen bonds formed by hydroxyl groups.

Table 4. The calculated HOMO–LUMO energy gaps and quantum chemical properties of title compound at DFT/B3LYP.

| No | Molecular Orbitals | Energy E | Energy Gap E | Ionization Potential I | Electron Affinity A | Global Hardness η | Chemical Potential μ | Electro-Negativity X | Global Softness σ | Global Electrophilicity ω |
|----|--------------------|----------|--------------|------------------------|---------------------|-------------------|----------------------|---------------------|----------------------|--------------------------|
| 1  | H                  | −6.62    | 5.68         | 6.62                   | 0.94                | 2.84              | −3.78                | 3.78                | 0.18                 | 2.52                     |
|    | L                  | −0.94    |              |                        |                     |                   |                      |                     |                      |                          |
| 2  | H – 1              | −7.30    | 7.74         | 7.30                   | 0.44                | 3.87              | −3.43                | 3.43                | 0.13                 | 1.53                     |
|    | L + 1              | 0.44     |              |                        |                     |                   |                      |                     |                      |                          |
| 3  | H – 2              | −7.42    | 8.15         | 7.42                   | 0.73                | 4.08              | −3.35                | 3.35                | 0.12                 | 1.38                     |
|    | L + 2              | 0.73     |              |                        |                     |                   |                      |                     |                      |                          |

H: HOMO, L: LUMO, I = −E_HOMO, A = −E_LUMO.

The UV-Vis spectrum of loganic acid is shown in Figure 5. The observed bands were assigned to the respective singlet and triplet electron levels calculated for the monomeric form of this compound—they are presented in Table 5.

Figure 5. Absorption and emission spectra of loganic acid.
Table 5. Calculated singlet and triplet electron levels of loganic acid in the monomeric form.

| Electron Levels | eV   | nm    | cm$^{-1}$ | Oscillator Strength |
|-----------------|------|-------|-----------|--------------------|
| **Singlets**    |      |       |           |                    |
| S1              | 5.1236 | 241.99 | 41,324 | 0.0073 |
| S2              | 5.3784 | 230.52 | 43,380 | 0.2038 |
| S3              | 5.8312 | 212.62 | 47,032 | 0.0182 |
| S4              | 5.8778 | 210.94 | 47,407 | 0.0516 |
| S5              | 6.2700 | 197.74 | 50,571 | 0.0001 |
| S6              | 6.3440 | 195.44 | 51,167 | 0.0008 |
| S7              | 6.4366 | 192.62 | 51,916 | 0.0041 |
| S8              | 6.5325 | 189.80 | 52,687 | 0.0020 |
| S9              | 6.5971 | 187.94 | 53,208 | 0.0020 |
| S10             | 6.6393 | 186.74 | 53,550 | 0.0004 |
| **Triplets**    |      |       |           |                    |
| T1              | 3.4084 | 363.76 | 27,491 | 0.0000 |
| T2              | 4.7521 | 260.90 | 38,329 | 0.0000 |
| T3              | 5.5947 | 221.61 | 45,124 | 0.0000 |
| T4              | 5.7579 | 215.33 | 46,440 | 0.0000 |
| T5              | 5.8279 | 212.74 | 47,006 | 0.0000 |
| T6              | 6.2618 | 198.00 | 50,505 | 0.0000 |
| T7              | 6.3102 | 196.48 | 50,896 | 0.0000 |
| T8              | 6.3757 | 194.46 | 51,424 | 0.0000 |
| T9              | 6.4022 | 193.66 | 51,637 | 0.0000 |
| T10             | 6.4411 | 192.49 | 51,951 | 0.0000 |

The wavelengths calculated for the monomeric form of loganic acid can be compared to those obtained for the dimer of this compound. The following fifteen singlet states were derived: characterized by their wavelength and oscillator strength (in parenthesis):

1. 249.2 (0.2459); 2. 246.8 (0.0027); 3. 245.9 (0.0001); 4. 244.6 (0.0000); 5. 240.8 (0.03165); 6. 239.3 (0.0093); 7. 225.6 (0.1780); 8. 224.8 (0.0023); 9. 223.8 (0.0915); 10. 222.3 (0.0009); 11. 218.1 (0.0004); 12. 217.4 (0.0058); 13. 213.9 (0.0002); 14. 213.5 (0.0024); 15. 213.4 (0.0034). The triplet state energies of the dimer are included in the range of 210–380 nm.

The comparison of the electron energies calculated for the monomer and dimer of loganic acid with the experimental values derived from the UV-Vis spectra allow us to draw the general conclusions of the electronic properties of the studied compound. The calculated energies of the singlet states fit well with those observed in the electronic spectra. The greatest oscillator strengths of these transitions appear for the singlet states located in the range of 200–260 nm and assigned to the bands at 260, 242, 230.5, 212.6, and 210.9 nm. In fact, the greatest intensity is exhibited by the bands observed in the absorption spectra (Figure 5) at 225 and 260 nm. These wavelengths fit well those reported for iridoid glycosides [47]. According to these data, the observed bands correspond to the HOMO→LUMO: $n$→$\pi^*$ transitions. These electron transitions are normally observed in the range of 200–600 nm. The theoretical HOMO→LUMO energy gap for loganic acid is 5.68 eV (45,812 cm$^{-1}$), i.e., at $\lambda = 218$ nm. Such a picture suggests that in the HOMO→LUMO excitation, the lone electron pair of the oxygen atom of the hydroxyl group substituted in
the cyclopenta[c]pyran system is transferred to the $\pi^*$ antibonding orbitals of the pyran ring of this system.

Such a scheme of these electron transitions is visible in the HOMO–LUMO picture shown in Figure 4. It should be noted that the experimental data fit well the results of the theoretical DFT calculations. The greatest oscillator strengths of the singlet transitions are foreseen in the range of 200–260 nm, which show a good accordance with the absorption bands observed at 225 and 260 nm, i.e., in a very narrow near-UV range. It explains why the color of loganic acid is white. As the range of near-UV is not visible to the human eye and this material scatters all the remaining wavelengths with nearly equal strength, it appears white.

The emission spectrum of loganic acid excited at 330 nm exhibits a strong band at 425 nm and several weak transitions on the slope of this broad band (Figure 5). The comparison of the absorption and emission spectra of loganic acid indicates that the Stokes shift for loganic acid is about 20,915 cm$^{-1}$.

3. Materials and Methods

Commercially available loganic acid (PubChem CID: 89640, purity HPLC $\geq$ 99%) synthesized by the method described in Ref. [48] were taken for measurements.

The attenuated total reflection–Fourier-transform infrared technique and Raman microscopy were used in the measurements of IR and Raman spectra recorded in the ranges of 50–4000 cm$^{-1}$ and 80–4000 cm$^{-1}$. IR spectra were measured using a Nicolet i550 (Thermo Scientific) spectrometer with a 2 cm$^{-1}$ accuracy. The Raman spectra were collected using a Renishaw InVia Raman spectrometer equipped with a confocal DM 2500 Leica optical microscope—the resolution was 2 cm$^{-1}$.

Room-temperature electron reflectance spectra were measured in the 200–1500 nm spectral range using a Cary-Varian 5E UV-VIS-near-IR spectrophotometer. The spectra were recorded with Praying Mantis diffuse reflectance accessories. In these measurements, the baseline was first recorded for Al$_2$O$_3$ powder, and this line was then subtracted from that obtained for particular powder sample spectra. The absorption spectra of the ground complexes in silicon paste were recorded.

Emission spectra and luminescence decay curves were recorded with a grating spectrophotograph (Princeton Instr. Model Acton 2500i) coupled to a streak camera (Hamamatsu Model C5680) operating in the 200–1100 nm spectral range with a temporal resolution of 20–100 ps. The luminescent properties of the complexes were investigated at room temperature.

The molecular structure of loganic acid was optimized at the DFT (Density Functional Theory) level using the Becker–Lee–Yang–Parr correlation functional and the 6–311G(2d,2p) basis set using the GAUSSIAN 03W program. The results of the DFT calculations were used in interpretation and analysis of the experimental spectroscopic studies. The mean square deviation between the experimental and calculated unscaled wavenumbers was nearly 25 cm$^{-1}$ for the IR and Raman spectra. The scaling of the calculated wavenumbers improved this result to 5 cm$^{-1}$ for the IR and 24 for the Raman spectra. A scaling factor of 0.96 was used for the range of 3700–2500 cm$^{-1}$ and 0.98 for the range of 2499–50 cm$^{-1}$ of the spectra.

4. Conclusions

Loganic acid appears in the solid state in a dimeric structure forming white small-crystalline powder. Its structural parameters were calculated using the DFT B3LYP/6–311G(2d,2p) approach. It was shown that these geometrical data fit well the structure of loganin determined in the XRD experiment.

IR and Raman spectra proved that loganic acid occurs in a dimeric form due to the existence of intermolecular $\text{C}^\text{OH} \cdots\text{O} \cdots\text{H}^\text{O} \cdots\text{C}$ hydrogen bonds between the adjacent molecules. It was confirmed by the DFT calculations carried out for both its monomeric
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and dimeric forms. The calculations carried out for these systems were the basis for the assignment of all the observed IR and Raman bands to the respective molecular vibrations.

The most characteristic vibrations observed in the vibrational spectra include those related to the C–O–C (i.e., θ-O-Φ) bridge bond. They were observed at the following wavenumbers: νas: 1150–1153 cm⁻¹; νs: 937–979 cm⁻¹; δ: 673–704 cm⁻¹, γ: 573–601 cm⁻¹, ω: 333 cm⁻¹; and τ: 115–175 cm⁻¹.

The atomic charges calculated using DFT proved that the C–O–C bridge has a strong polar character due to clear positive charges on the carbon atoms and the negative charge of the oxygen atom.

The electron properties of loganic acid are dominated by the electronic structure of the double cyclopentane-pyran system. In the HOMO→LUMO excitation, the lone electron pairs of the oxygen atoms from the hydroxyl groups are transferred to π* antibonding orbitals. The n(O)→π* transition corresponds to the strong and broad band observed both in the UV-Vis and luminescence spectra of this compound.

The composition and electron structure of loganic acid suggest that this compound can be used as a complexing ligand binding the d-electron and f-electron metal ions. The binding of such ions can be fulfilled by carboxyl and OH groups of the ligands. The energies of the singlet and triplet levels determined for loganic acid are convenient for its excitation and energy transfer to a metal ion.

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