Structure–Property Relationships of Dibenzylidenecyclohexanones

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ABSTRACT: A series of symmetrical dibenzylidene derivatives of cyclohexanone were synthesized with the goal of studying the physicochemical properties of cross-conjugated dienones (ketocyanine dyes). The structures of the products were established and studied by X-ray diffraction, NMR spectroscopy, and electronic spectroscopy. All products had the $E,E$-geometry. The oxidation and reduction potentials of the dienones were determined by cyclic voltammetry. The potentials were shown to depend on the nature, position, and number of substituents in the benzene rings. A linear correlation was found between the difference of the electrochemical oxidation and reduction potentials and the energy of the long-wavelength absorption maximum. This correlation can be employed to analyze the properties of other compounds of this type. The frontier orbital energies and the vertical absorption and emission transitions were calculated using quantum chemistry. The results are in good agreement with experimental redox potentials and spectroscopic data.

1. INTRODUCTION

The enormous synthetic potential of the carbon–carbon double bond conjugated with the carbonyl group has long and successfully been utilized in organic chemistry.1,2 The introduction of two double bonds in conjugation with the keto group enables some additional transformations.3 These compounds, called cross-conjugated dienones, ketocyanine dyes, or (more rarely) diarylidene derivatives of ketones, attract the attention of researchers due to diverse synthetic chemistry and extensive scope of applicability, first of all, in biology and medicine.4–6 Recently, cross-conjugated dienones with pyridine substituents have started to be used as ligands for the preparation of discrete and polymeric coordination compounds.7–9

Apart from participating in addition reactions, the dienone double bonds account for two more features of this class of compounds. First, an intrinsic feature of dienones is that they exist as $E$- and $Z$-isomers, with interconversion between them being induced by various factors such as light, acids, and complex formation with transition metals.10–14 Most often, E,E-isomers are most stable for cyclopentanone and cyclohexanone derivatives. The percentage of $E,Z$- and $Z,Z$-isomers increases with increasing ring size.4,12

One more important feature of carbonyl-conjugated double bonds is the ability to undergo [2+2]-photocycloaddition (PCA) reactions.12,15,16 Furthermore, in the case of free dienones, transformations of this type can occur both in the crystal and in solution. The possibility and stereoselectivity of PCA can both be controlled by supramolecular preorganization of double bonds, i.e., by creating the most appropriate geometry of the preceding dimer.17–19 In the case of pyridine derivatives in the crystal, this can be accomplished by supramolecular templating by metal complexes,20 resorcinol (pyridine-containing mono-enones21 and acyclic dienones22) or by treatment with silver ions (only pyridine-containing acyclic dienones were studied).23

Within the framework of the project on the design of photoswitchable supramolecular systems, we started a comprehensive targeted investigation of cross-conjugated dienones containing ionophoric substituents such as crown ethers.24 The idea of this study was to generate hybrid molecules combining two functional components: an iono-phoric group capable of coordination to metal ions,
ammonium ions, or other analytes and a photoswitchable group providing control of the coordination by exposure to external light. For a more in-depth understanding of the photochemical reactions that take place, it is necessary to study in detail the properties and physicochemical characteristics of model compounds. In addition, it is necessary to establish the possibility of conducting the PCA reaction in the crystal and in solution without supramolecular preorganization of the reacting double bonds (Figure 1).

Here, we report the synthesis and study of dienones 1a–f, which differ in the nature and the number of alkylthio, dialkylamino, and alkoxy substituents. These structures are chromophoric models of crown ethers and aza/thia-crown ethers. As the central moiety, we choose cyclohexanone to draw an analogy with cyclopentanone derivative 2 addressed in our previous study.25

The structures of compounds were established by X-ray diffraction analysis and were studied by NMR spectroscopy and electronic spectroscopy. An X-ray diffraction study was used to find out how favorable the double bonds of neighboring molecules are arranged for PCA to occur in the crystal without a supramolecular action. Cyclic voltammetry (CV) measurements were carried out to find the oxidation and reduction potentials, which were used to elucidate the dependence of the energy characteristics of molecules on the position, nature, and number of substituents in the benzene rings. Also, we attempted to find a correlation between the photophysical and electrochemical characteristics of dienones 1a–f.
solution with crystallographic data for the whole series, since the crystals of high quality are not available for all compounds. In the case of dienones, it is especially important to explore their conformational behavior in solutions, which is important for prediction and determination of the structures of supramolecular systems based on bis-crown-containing dienones. Therefore, we studied the structural characteristics of (E,E)-dienones 1d and 2 using various NMR techniques.

In the crystalline state, (E,E)-tetramethoxydienone 1d and (E,E)-tetramethoxydienone 2 exist as nearly planar unsymmetrical syn,anti- and symmetrical syn,syn-conformers, respectively, which is apparently caused by the requirement for close packing of molecules. On going to solutions, fast conformational equilibrium between symmetrical syn,syn-, anti,anti- and unsymmetrical syn,anti-conformers may be established (Figure 3) by analogy with the previously studied bis-crown-containing stilbenes and distyrylbenzenes.

The nuclear Overhauser effect spectroscopy (NOESY) spectra of compounds 1d and 2 in CD2Cl2, which are shown in Figures S1 and S2 (the atom numbering differing from the IUPAC rules is presented in Figure 1), exhibit averaged signals from various conformers. The spectrum of dienone 1d displays an intense cross-peak, corresponding to the intramolecular through-space interaction between the H(2′) protons of the benzene ring and the H(3) methylene protons of the cyclohexanone moiety, and a weak cross-peak between the H(6′) aromatic protons and the H(α) protons of ethylene bonds. These types of coupling are inherent in the syn,syn-conformer. Apart from the indicated cross-peaks, a cross-peak between the H(6′) aromatic protons and the H(3) methylene protons of the cyclohexanone moiety is present in the NOESY spectrum. However, it is worth mentioning that the spectrum does not show a cross-peak between the H(2′) protons of the benzene ring and the H(α) protons of the ethylene bonds (Figure S1). The absence of this cross-peak in the spectrum can be explained by assuming that mainly syn,syn,(syn/anti)-conformers are involved in equilibrium. The contribution of H(2′)−H(α) coupling in the syn,anti-conformer to the overall spectral pattern is lower, as only one of the two H(α) protons of the ethylene bond is coupled with H(2′).

Figure 2. Molecular structure and atom numbering for crystals of 1a–e.
The NOESY spectrum of dienone 2 showed similar interactions: intense cross-peaks corresponding to the intramolecular coupling of the H(2′) and H(6′) protons of the benzene ring with the H(3) methylene protons of the cyclopentanone moiety and the cross-peak between the H(6′) aromatic protons and the H(α) protons of the ethylene bonds (Figure S2).

Although the NOESY spectra do not make it possible to accurately determine the contribution of each conformer of 1d and 2 to the equilibrium due to the strong coupling of methylene protons with both H(2′) and H(6′) type protons in all conformers, the spectral details still provide the conclusion that a mixture of syn,(syn/anti)-conformers is present predominantly.

An indirect indication of the predominance of syn,(syn/anti)-conformers in solution can also be derived from a comparison of the positions of signals for the H(2′) and H(6′) benzene protons, which are located in the ortho-position to the ethylene substituent. The H(2′) type protons are also located in the ortho-position to the electron-donating methoxy group and, in principle, should resonate in a higher field than H(6′) located in the para-position.

The theoretical ratio between three possible conformers for each dienone was calculated from the energies of the stable structures of these compounds found using the FireFly software package (Figure 3).

The 1H NMR spectra of conformers of (E,E)-dienones 1d and 2, calculated with allowance for their mole fractions, are in good agreement with experimental data (Table 2), in

### Table 1. Selected Geometric Parameters (Bond Length d, Å; Bond Angle ω, deg, and Torsion Angle τ, deg) for the Molecules of 1a–e

| parameter | 1a | 1b | 1c<sup>a</sup> | 1d<sup>a</sup> | 1e |
|-----------|----|----|---------------|---------------|----|
| d1        | 1.230(1) | 1.231(1) | 1.232(9) | 1.240(2) | 1.228(s) |
|           | 1.235(9) | 1.227(2) | 1.499(3) | 1.495(3) |               |
|           | 1.501(1) | 1.502(2) | 1.491(3) | 1.495(3) |               |
|           | 1.496(11) | 1.490(11) | 1.502(3) |                 |               |
|           | 1.344(1) | 1.352(2) | 1.333(10) | 1.343(3) | 1.345(3) |
|           | 1.348(1) | 1.350(2) | 1.351(11) | 1.345(3) |               |
|           | 1.371(10) | 1.373(11) | 1.346(3) |                 |               |
|           | 1.470(1) | 1.461(1) | 1.453(10) | 1.461(3) | 1.462(3) |
|           | 1.468(1) | 1.462(1) | 1.358(11) | 1.459(3) |               |
|           | 1.443(10) | 1.434(11) | 1.463(3) |                 |               |
|           | 120.07(9) | 120.75(9) | 120.9(7) | 120.1(2) | 120.85(15) |
|           | 120.97(9) | 120.37(9) | 119.1(7) | 120.2(2) |               |
|           | 116.3(8) | 115.47(9) | 117.6(6) | 116.7(2) | 116.8(2) |
|           | 115.34(9) | 116.50(9) | 118.1(7) | 117.3(2) |               |
|           | 116.2(6) | 116.0(7) | 116.3(2) |                 |               |
|           | 128.92(9) | 132.1(1) | 133.1(6) | 130.9(2) | 130.6(2) |
|           | 130.17(9) | 130.2(1) | 134.3(7) | 129.7(2) |               |
|           | 132.3(6) | 131.1(6) | 130.2(2) | 130.4(2) |               |
|           | 122.57(9) | 126.19(9) | 127.0(7) | 124.7(2) | 125.7(2) |
|           | 124.67(9) | 125.36(9) | 127.3(7) | 123.8(2) |               |
|           | 125.3(6) | 125.2(7) | 124.2(2) | 125.8(2) |               |
| r1-2-3    | −18.9(1) | 6.8(2) | 7(1) | 3.7(3) | −4.5(3) |
|           | 11.0(1) | 2.5(2) | −6(1) | −9.6(3) | 4.5(3) |
|           | 8(1) | −9(1) | −5.3(3) |                 |               |
|           | −172.8(7) | 174.1(8) | 179.6(1) | 179.4(2) |               |
| r2-3-4    | 177.5(1) | 178(1) | 179.5(8) | 176.1(2) |               |
|           | 177.8(1) | 180(1) | −176.5(2) |                 |               |

<sup>a</sup>Data are given for two independent molecules.
particular, the H(2′) ortho-proton has a greater chemical shift than the H(6′) ortho-proton. Thus, quantum chemical data are in good agreement with the experimental data.

2.4. Electrochemistry. With the goal to elucidate the effect of substituents in the aromatic rings of cyclohexanone-based cross-conjugated dienones on the energy of frontier orbitals and to compare the results with these parameters of cyclopentanone-based dienones described previously, we studied compounds 1a–f by cyclic voltammetry (CV) on a cleaned glassy carbon (GC) electrode in MeCN solutions. The CV curves were measured from 0 V toward the cathode or anode potential region. Table 3 presents the first peak potentials determined in MeCN to compare the electrochemical parameters with the data obtained by other physicochemical methods in the same solvent. The table also presents the differences (shifts) of the reduction and oxidation potentials of the substrates in comparison with unsubstituted compound 1a.

We calculated the vertical ionization potentials (IPs) and electron affinities (EAs) of the dyes. We have found that electron detachment takes place from the highest occupied molecular orbital (HOMO)−1, while the electron attachment occurs to the lowest unoccupied molecular orbital (LUMO). The IPs and EAs are also given in Table 3. The values correlate with the oxidation and reduction potentials and well reproduce the trend in the series (shift with respect to 1a).

The first cathodic peaks of compounds 1a–f are single electron and are irreversible, but the reverse peak current is markedly lower (Figure 4a). The cathodic peak potentials of cyclohexadienones are shifted to the cathodic side compared to the potentials of the corresponding substituted cyclopentadienones, which may be indicative of a lower degree of conjugation between C==O and C==C fragments of

| Table 2. Proton Chemical Shifts of Compounds 1d and 2 Averaged Taking into Account the Mole Fractions of Conformers in Comparison with Experimental Data (in MeCN-d3) |
|---|---|---|---|---|---|---|
| protons | 1d experiment | 1d calculation | 2 experiment | 2 calculation |
| C(4)H2 | 1.82 | 1.92 | 2.98 | 3.22 |
| C(3)H2 | 2.98 | 3.22 | 3.15 | 3.25 |
| H(5′) | 7.00 | 6.84 | 7.05 | 6.87 |
| H(2′) | 7.14 | 7.32 | 7.26 | 7.22 |
| H(6′) | 7.17 | 7.75 | 7.28 | 7.39 |
| CHAr (α) | 7.66 | 8.36 | 7.44 | 7.74 |

| Table 3. Electrochemical Potentials of Compounds 1a–f (C = 1 × 10⁻⁴ mol L⁻¹) in MeCN Measured by CV Relative to Ag/AgCl/KCl (sat.) in the Presence of 0.1 M Bu₄NClO₄ on a GC Electrode (Potential Sweep Rate of 200 mV s⁻¹) and Frontier Orbital Energies Calculated by Quantum Chemistry |
|---|---|---|---|---|---|---|---|---|---|
| R¹, R² | E_red, V | EA, eV | ΔE_red, mV (ΔEA) | E_red, V | IP, eV | ΔE_red, mV (ΔIP) | ΔE = E_red − E_{EA}, V | EA−IP, eV |
| 1a | H, H | −1.38 | 2.642 | 0 | 2.02 | 6.291 | 0 | 3.40 | 3.649 |
| 1b | OMe, H | −1.51 | 2.513 | 130 (129) | 1.52 | 5.840 | 500 (451) | 3.03 | 3.327 |
| 1c | SMe, H | −1.39 | 2.618 | 10 (24) | 1.33 | 5.724 | 690 (567) | 2.72 | 3.106 |
| 1d | OMe, OMe | −1.46 | 2.524 | 80 (118) | 1.53 | 5.695 | 490 (596) | 2.99 | 3.171 |
| 1e | NMe₂, H | −1.63 | 2.316 | 250 (326) | 0.87 | 5.098 | 1150 (1193) | 2.50 | 2.782 |
| 1f | NEt₂, H | −1.64 | 2.304 | 260 (338) | 0.86 | 5.059 | 1160 (1232) | 2.50 | 2.755 |

*a*Shift of the reduction potentials relative to those of 1a. *b*Shift of the oxidation potentials relative to those of 1a.
dibenzylidenecyclohexanone derivatives compared to analogous cyclopentanone derivatives.

The range of differences between the first cathodic peak potentials of dienones 1b−f and unsubstituted dienone 1a is rather broad (−10 to 260 mV, Table 3 and Figure 4a). The most pronounced and comparable effects on the cathodic potentials are made by electron-donating dimethyl- and diethylamino groups: the potentials of 1e and 1f shift to the cathodic region by 250 and 260 mV, respectively. The effects of one and two methoxy groups in this series are much less pronounced (130 and 80 mV, respectively). The methylthio group exerts a negligibly low electron-donating effect (10 mV).

The effect of substituents on the electrooxidation of dienones 1b−f in comparison with unsubstituted 1a was much more pronounced. The potential shifts to the less anodic region were 490−1150 mV (Table 3; see Figure 4b). The most pronounced shift was observed for dienones 1e and 1f containing dimethyl- and diethylamino groups; the oxidation potentials of these compounds were close to the corresponding values for amines (0.8−1.1 V).35

These considerable differences between the anodic potentials of substituted dienones 1b−f and unsubstituted dienone 1a indicate that the HOMO and HOMO − 1 are more localized on the electron-donating substituents of the conjugated π-system (see Figures S3−S7 of the Supporting Information).

Comparison of the electrochemical behaviors of dibenzylidenecyclohexanone derivatives containing para-dimethylamino groups in benzene rings revealed the shift of the first reduction peaks to a more cathodic region (−1.38 and −1.63 V, respectively). This fact attests to a decrease in the degree of π-conjugation on going from the five-membered to the six-membered ring. In less conjugated compound 1e, the electron density is localized to a higher extent on the dimethylamino group, and oxidation occurs at a lower anodic potential. For compounds with a five-membered ring, the anodic potential increases with increasing degree of conjugation (0.87 and 0.93, respectively) due to increasing transfer of π-electron density toward the carbonyl group. It is worth noting that dimethyl- and diethylamino-dibenzylidenecyclohexanone derivatives 1e and 1f are reduced at virtually identical potentials (Figure 5), whereas, for more conjugated cyclopentanone analogues, the difference between the cathodic potentials is 150 mV.25

2.5. Photophysics. With the goal of determining the effect of substituents on the spectral properties of dienones, we recorded the electronic absorption and fluorescence spectra of 1a−f (Table 4 and Figure 6).

All dienones show an intense long-wavelength absorption band (LAB) (λmax from 326 nm for 1a to 445 nm for 1f) and several more bands at shorter wavelengths. The LABs can be assigned to HOMO–LUMO type transitions,36,37 and the shorter-wavelength bands correspond to local electron transitions within the aromatic rings. Note the qualitative dependence of the LAB maximum position on the electron-donating ability of the para-substituents in benzylidene moieties. The LAB of para-diethylamino-substituted 1e,f is most red-shifted relative to that of unsubstituted 1a, which is in good agreement with the high electron-donating ability of substituents and correlates with the lowest (among the given series of compounds) oxidation potentials (Table 3). In the
Table 4. Parameters of the Electronic Absorption and Fluorescence Spectra of Dienones 1a–f in MeCN

| Dienone | λabs (ε) nm (μmol⁻¹·dm³·cm⁻¹) | λf/ε nm |
|---------|---------------------------------|--------|
|         | experiment | calculation (oscillator strength) | experiment | calculation (oscillator strength, τrad ns) |
| 1a      | 326 (31 500) | 381 (0.03) | 1736 (0.005, 8826) |
| 1b      | 356 (37 000) | 390 (1.14) | 848 (0.03, 323) |
| 1c      | 368 (43 000) | 417 (1.27) | 620 (0.11, 51) |
| 1d      | 370 (36 000) | 411 (1.10) | 878 (0.03, 414) |
| 1e      | 431 (45 400) | 454 (1.53) | 620 (0.11, 51) |
| 1f      | 445 (56 000) | 461 (1.64) | 620 (0.11, 51) |

Table 5. Relative Energies of (E,E), (E,Z), and (Z,Z) Isomers of the Dienones 1a–f in the S1 State

| Dienone | (E,E) | (E,Z) | (Z,Z) |
|---------|-------|-------|-------|
| 1a      | 0.00  | −6.00 | −1.44 |
| 1b      | 0.00  | −4.86 | −0.96 |
| 1c      | 0.00  | −2.22 | 0.92  |
| 1d      | 0.00  | −6.98 | −1.66 |
| 1e      | 0.00  | 5.39  | 6.15  |
| 1f      | 0.00  | 5.45  | 6.15  |

Figure 6. Absorption spectra of dienones 1a–f, in MeCN, C = 1 × 10⁻⁶ mol L⁻¹.

state, the excited S1 state is not always dominated by the (E,E) isomers. Only in 1e and 1f, (E,E) isomer has the lowest energy in the S1 state, with (E,Z) and (Z,Z) isomers lying noticeably higher. This means that the excited 1e and 1f relax to their (E,E) isomers, which emit at 478 and 485 nm, respectively, with high oscillator strengths and, therefore, short radiative lifetimes (2 ns). In other dienones, the excited state is dominated by the (E,Z) isomer with small oscillator strength and long radiative lifetime (from S1 ns and more). Such long radiative lifetime allows the molecule to relax nonradiatively. Obviously, the barrier from the (E,E) to (E,Z) isomer is sufficiently small so that the isomerization proceeds rather fast.

Characteristic features of the absorption and emission of compound 1f and itsaza-crown ether analogue are described in our publication.⁴⁰

2.6. Correlations. Previously, we studied the dependences of a number of calculated and experimental characteristics for a broad range of N-donor ligands, including some pyridine-containing dienones. In particular, we identified a linear dependence between the electrochemical and spectrophotometric characteristics of dienone molecules.³¹,⁴²

Here, we performed a correlation analysis (Figure 8) between the energy of the long-wavelength absorption maximum and the oxidation/reduction potential difference to reveal the possible correlation of the electrochemical and optical data with the electronic properties of substituents in the benzene rings of 1a–f.

The observed correlation is not surprising because both oxidation/reduction involves frontier orbitals, and excitation LAB is a HOMO–LUMO transition. Our direct calculations of vertical ionization potential and electron affinity show that the electron is attached to LUMO, while electron detachment takes place from HOMO − 1, which is quasi-degenerate with HOMO. We note the fact that solvation slightly affects the correlations between the redox and optical properties. Although the effect of solvation is different for the excitation energy, IP, and EA, the solvation effects in the series differ slightly, which retains the correlation.

These results indicate that, despite the irreversibility of electrochemical reduction, the energy characteristics of the frontier orbitals in a series of related compounds such as cross-conjugated dienones can be adequately described by both electrochemical and spectrophotometric data. The results of this study could be useful for analysis of new diene-type compounds and for the design of required characteristics of molecules.

3. CONCLUSIONS

The products of cyclohexanone condensation with benzaldehyde derivatives tend to exist as E,E-isomers. The conformational analysis of (E,E)-dienes using X-ray diffraction and
NMR data revealed their structural features in the crystalline state and in solution. More favorable syn, (syn/anti)-conformations of the conjugated moieties of dibenzylidenecyclohexanones containing four methoxy groups were confirmed by quantum chemical calculations. It was found that the solid-state PCA reaction of compounds 1a–e requires the use of a supramolecular template. The spectral properties of dienone derivatives 1a–f were compared considering their electronic spectra. Using quantum chemical calculations, the absence of fluorescence of 1a was explained by the fact that the lowest excited state of 1a is $\pi-\pi^*$ dark state, whereas in 1b–f, it is $\pi-\pi^*$ bright state. The obtained dependences of the redox potentials on the position, nature, and number of substituents in the benzene ring and their correlation with photophysical and quantum chemical characteristics are useful for the subsequent studies of photoactive dienone derivatives. The structures and properties of cyclohexanone-based dienones can also be used to design photoactive supramolecular systems.

4. EXPERIMENTAL SECTION

4.1. Materials. MeCN (extra high purity, water content <0.3%, Cryochrom) was used to prepare solutions. Bu$_4$NClO$_4$ (≥99%, for electrochemical analysis) was purchased from Sigma-Aldrich and used as a background electrolyte. Cyclohexanone, cyclopentanone, benzaldehyde, 4-methoxybenzaldehyde, 3,4-dimethoxybenzaldehyde, 4-(methylthio)-benzaldehyde, 4-dimethylaminobenzaldehyde, and 4-diethylaminobenzaldehyde (Sigma-Aldrich) were used as received. EtOH (chemically pure) was used without additional purification, and (2E,6E)-2,6-bis(3,4-dimethoxybenzylidene)cyclopentanone (2) was prepared as described previously.25 DC-Alufolien Aluminiumoxid 60 F$_{254}$ neutral was purchased from Merck.

4.1.1. Synthesis of 2,6-Dibenzylidenecyclohexanone Derivatives 1a–f (General Procedure). Ethanol (1 mL) and a 10% aqueous solution of NaOH (1 mL) were mixed in a round-bottom flask. A mixture of aldehyde (2 mmol) and cyclohexanone (1 mmol) in EtOH (2 mL) was prepared separately, and a half of this mixture was added with vigorous stirring until the reaction was over (thin-layer chromatography, TLC monitoring). The precipitate that formed was collected on a filter, thoroughly washed with an EtOH–water mixture (1:1 v/v), then with water, and again with an EtOH–water mixture (1:1 v/v), and dried in air.

Pale-yellow fine crystalline powder. Yield: 90%, mp: 118–120 °C (cf. ref 26: 116–118 °C). $^1$H NMR (δ, ppm, /Hz): 1.80 (m, 2 H, C(4)H$_2$), 2.96 (m, 4 H, C(3)H$_2$, C(S)H$_2$), 7.38–7.41 (m, 4 H, 2 H(3′), 2 H(5′)), 7.47 (m, 2 H, 2 H(4′)), 7.55 (m, 4 H, 2 H(2′), 2 H(6′)), 7.72 (s, 2 H, 2 CHPh). Calcd for C$_{20}$H$_{18}$O (274.36): C, 87.56; H, 6.61.

Figure 7. Orbitals involved in the first electron transition of dienone 1a, oxidation and reduction.

Figure 8. Correlation between the energy of the long-wavelength absorption maximum and the difference of oxidation/reduction potentials for dienones 1a–f.
Table 6. Crystallographic Characteristics and X-ray Experiment Details for 1a–c

| diene | 1a | 1b | 1c |
|-------|----|----|----|
| molecular formula | C_{20}H_{18}O | C_{22}H_{22}O_3 | C_{22}H_{22}O_5 |
| molecular weight, g mol^{-1} | 274.34 | 334.40 | 366.51 |
| crystal system | monoclinic | monoclinic | monoclinic |
| space group | P2_1/c | P2_1/c | P2_1/n |
| a, Å | 9.4669(3) | 8.8899(3) | 9.2176(11) |
| b, Å | 18.2488(7) | 9.4022(3) | 22.382(3) |
| c, Å | 9.3371(3) | 20.6943(7) | 18.333(2) |
| α, deg | 90.00 | 90.00 | 90.00 |
| β, deg | 115.2690(10) | 100.1720(10) | 103.619(2) |
| γ, deg | 90.00 | 90.00 | 90.00 |
| V, Å^3 | 1458.72(9) | 1702.54(10) | 3675.8(8) |
| Z | 4 | 8 | 8 |
| \(\rho_{\text{calc}}\) g cm^{-3} | 1.249 | 1.305 | 1.325 |
| F(000) | 5840 | 7120 | 15520 |
| \(\mu\) (Mo Kα), mm^{-1} | 0.075 | 0.086 | 0.297 |
| crystal size, mm | 0.44 × 0.36 × 0.32 | 0.38 × 0.22 × 0.20 | 0.46 × 0.26 × 0.02 |
| scan range on 2θ, deg. | 4.76–58.00 | 4.66–58.00 | 2.92–52.00 |
| index range | \(-12 \leq h \leq 12, \ -24 \leq k \leq 24, \ -12 \leq l \leq 12\) | \(-12 \leq h \leq 12, \ -12 \leq k \leq 12, \ -28 \leq l \leq 28\) | \(-11 \leq h \leq 11, \ -27 \leq k \leq 27, \ -22 \leq l \leq 22\) |
| number of independent refl. \([R_{\text{int}}]\) | 3830 [0.0240] | 4522 [0.0266] | 7225 [0.1062] |
| number of refl with I > 2σ(I) | 3227 | 3697 | 3673 |
| number of variables | 190 | 228 | 455 |
| R indices for I > 2σ(I) | \(R_I = 0.0403, wR_2 = 0.1082\) | \(R_I = 0.0403, wR_2 = 0.1071\) | \(R_I = 0.1075, wR_2 = 0.2960\) |
| R indices for all refl. | \(R_I = 0.0483, wR_2 = 0.1122\) | \(R_I = 0.0513, wR_2 = 0.1129\) | \(R_I = 0.1898, wR_2 = 0.3240\) |
| GOOF | 1.061 | 1.037 | 1.062 |
| residuals, min/max, e Å^{-3} | -0.23/0.32 | -0.21/0.38 | -0.48/1.11 |
Table 7. Crystallographic Characteristics and X-ray Experiment Details for 1d and 1e

| dieneone | 1d | 1e |
|----------|----|----|
| molecular formula | C$_{24}$H$_{26}$O$_5$ | C$_{25}$H$_{28}$N$_2$O |
| molecular weight, g mol$^{-1}$ | 394.45 | 360.48 |
| crystal system | monoclinic | orthorhombic |
| space group | P2$_1$/n | Cmcm |
| a, Å | 8.6522(8) | 21.798(4) |
| b, Å | 32.232(3) | 8.9774(16) |
| c, Å | 14.3606(13) | 9.6932(17) |
| α, deg | 90.00 | 90.00 |
| β, deg | 90.00 | 90.00 |
| γ, deg | 90.00 | 90.00 |
| V, Å$^3$ | 3973.6(6) | 1896.8(6) |
| Z | 8 | 4 |
| $β_{dib}$ g·sm$^{-3}$ | 1.319 | 1.262 |
| F(000) | 1680.0 | 776.0 |
| μ(Mo Kα), mm$^{-1}$ | 0.092 | 0.077 |
| crystal size, mm | 0.52 × 0.43 × 0.02 | 0.44 × 0.21 × 0.04 |
| scan range on 2θ, deg | 3.12–58.00 | 4.91–57.99 |
| index range | −11 ≤ h ≤ 11, −43 ≤ k ≤ 43, −19 ≤ l ≤ 19 | −29 ≤ h ≤ 29, −12 ≤ k ≤ 12, −13 ≤ l ≤ 13 |
| number of measured refl. | 43363 | 9168 |
| number of independent refl. [R(int)] | 10564 [0.0732] | 2730 [R(int) = 0.0557] |
| number of refl with I > 2σ(I) | 6213 | 2076 |
| number of variables | 531 | 129 |
| R indices for I > 2σ(I) | $R_I = 0.0595, wR_2 = 0.1271$ | $R_I = 0.0474, wR_2 = 0.1000$ |
| R indices for all refl. | $R_I = 0.1212, wR_2 = 0.1415$ | $R_I = 0.0762, wR_2 = 0.1138$ |
| GOOF | 1.013 | 1.023 |
| residuals, min/max, e Å$^{-3}$ | −0.23/0.25 | −0.24/0.17 |
| flack parameter | 2(2) |

Found: C, 87.74; H, 6.35. UV–vis (MeCN) $λ_{max}$ 231 nm ($ε = 14.700 M^{-1}·cm^{-1}$), 326 nm ($ε = 31.500 M^{-1}·cm^{-1}$).

4.1.1.5. (2E,6E)-2,6-Bis[4-(dimethylamino)benzylidene]cyclohexanone (1e). Yellow-orange fine crystalline powder. Yield: 52%, mp: 218–220 °C (cf. ref 28: 240–242 °C). 1H NMR (δ, ppm, J/Hz): 1.73 (m, 2 H, C(4)H$_2$), 2.94 (m, 4 H, C(3)H$_2$, C(5)H$_2$), 3.85 (s, 6 H, 2 MeO), 7.01 (d, 4 H, 2 H(3′), 2 H(5′), $J = 8.8$), 7.53 (d, 4 H, 2 H(2′), 2 H(6′), $J = 8.8$), 7.67 (s, 2 H, 2 CHAr). Calcd for C$_{25}$H$_{28}$N$_2$O$_3$ (360.49): C, 79.96; H, 7.83; N, 7.77. Found: C, 79.78; H, 7.71; N, 7.57%. UV–vis (MeCN) $λ_{max}$ 270 nm ($ε = 17.400 M^{-1}·cm^{-1}$), 431 nm ($ε = 45.400 mol^{-1}·dm^{-3}·cm^{-1}$); fluorescence (MeCN, $λ_{ex}$ 428 nm) $λ_{max}^{fl}$ 563 nm.

4.1.1.6. (2E,6E)-2,6-Bis[4-(diethylamino)benzylidene]cyclohexanone (1f). Dark orange crystalline powder. Yield: 12%, mp: 167–170 °C (cf. ref 29: 144–145 °C). 1H NMR (δ, ppm, J/Hz): 1.17 (t, 12 H, 4 Me, $J = 7.1$), 1.82 (m, 2 H, C(4)H$_2$), 2.84 (m, 4 H, C(3)H$_2$, C(5)H$_2$), 3.44 (q, 8 H, 4 CH$_2$Me, $J = 7.1$), 6.75 (d, 2 H, 2 H(3′), 2 H(5′), $J = 8.9$), 7.44 (d, 4 H, 2 H(2′), 2 H(6′), $J = 8.9$), 7.60 (s, 2 H, 2 CHAr). Calcd for C$_{25}$H$_{28}$N$_2$O$_3$ (416.60): C, 80.73; H, 8.71; N, 6.72. Found: C, 80.56; H, 8.75; N, 6.62%. UV–vis (MeCN) $λ_{max}$ 276 nm ($ε = 22.300 M^{-1}·cm^{-1}$), 445 nm ($ε = 56.000 mol^{-1}·dm^{-3}·cm^{-1}$); fluorescence (MeCN, $λ_{ex}$ 440 nm) $λ_{max}^{fl}$ 562 nm.

4.2. Methods. The reactions were monitored by thin-layer chromatography using DC-Alufolien Aluminiumoxid 60 F$_{254}$ neutral plates, Merck. Melting points (uncorrected) were measured on a Mel-Temp II instrument. 1H NMR spectra were recorded on a Bruker DRX-500 spectrometer (operating at 500.13 MHz) in MeCN-$d_4$ at 25–30 °C using the solvent signal as the internal standard ($δ_H$ 1.96 ppm). The chemical shifts were determined with an accuracy of 0.01 ppm, and the spin–spin coupling constants were determined with an accuracy of 0.1 Hz.

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The electronic absorption spectra were measured on a Cary 4000 spectrophotometer in MeCN. Fluorescence spectra were obtained on a Cary Eclipse spectrophuorimeter at room temperature. All manipulations with solution dyes 1a–f were performed in a darkroom under red light (daylight induces the E–Z photoisomerization).

4.3. Cyclic Voltammetry. The electrochemical measurements were carried out using an IPC Pro M potentiostat in a three-electrode system. A glassy carbon disk (d = 2 mm) served as the working electrode, a 0.1 M Bu4NClO4 solution in MeCN was used as the supporting electrolyte, and Ag/AgCl/KCl (aq. sat.) reference electrode and a platinum plate auxiliary electrode were used. The working electrode surface was polished by alumina powder with a particle size of less than 0.5 μm (Sigma-Aldrich). In the CV measurements, the potential sweep rate was 100 mV s⁻¹. The potentials are presented with iR-compensation. The number of transferred electrons was determined by comparing the peak current in the substrate and the current of single-electron oxidation of ferrocene taken in the same concentration. Concentration of substrate and the current of single-electron oxidation were presented with iR.

The radiative lifetimes were calculated using the given formula:

\[ \tau_i = 1/k_i \]

where \( x_i \) is the mole fraction of the ith conformer and \( E_i \) is the ground state energy of this conformer. The calculated UV–vis absorption and emission properties of the rotamers are almost the same (within 2 nm); therefore, we give only the values for the lowest energy conformer in the respective state: (syn,syn)-conformer for the absorption from the ground state and (anti,anti)-conformer for the emission from the S1 excited state.

The vertical ionization potentials (IPs) and electron affinities (EAs) were calculated by restricted open-shell DFT (RO-DFT) for the corresponding monocation and monoaion of each dye. The functional, basis set and solvation model were the same.

1H NMR spectra were calculated using a Prioda program package with the PBE functional and triple-ζ quality basis set. The optimized geometries were taken from the PBE0/6-31+G(d,p)/DPCM calculation. Previously, we have shown that for dienones, solvent effects are important to properly reproduce the structures and conformation energies.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06129.

Crystallographic data (CIF)
Crystallographic data (CIF)
Crystallographic data (CIF)
Crystallographic data (CIF)
Crystallographic data (CIF)

NOESY spectra of compounds 1d and 2 in CD2Cl2 (Figures S1 and S2); cyclic voltammogram 1a (Figure S3); fluorescence spectra of compounds 1e,f (Figure S4); quantum chemical calculations, orbitals involved in the first electron transition of compounds 1b–f (Figures S5–S9); and correlations between the calculated frontier orbital energies, ionization potential and electron affinities, and experimental oxidation and reduction potentials (Figures S10–S12) (PDF)

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Notes
The authors declare no competing financial interest.

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