The Crystal Structure of a Squarylium Dye, 2,4-Bis(1,3,3-trimethyl-2-indolinylidenemethyl)cyclobutenediylium-1,3-diolate

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(Received August 6, 1985)

Synopsis.   The crystal structure of 2,4-bis(1,3,3-trimethyl-2-indolinylidenemethyl)cyclobutenediylium-1,3-diolate has been determined. The space group is $P2_1/c$, with a=9.5115(4), b=15.712(1), c=15.174(1) Å, β=96.138(5)°, and Z=4. The molecule adopts the trans conformation.

With interest increasing in squarylium dyes as materials for effective photovoltaic devices, much attention has been paid to their solid-state structure. According to Morel et al.,[1] devices with squarylium dyes containing indoline rings have an especially high short-circuit-photocurrent yield. In order to reveal the structural feature of such compounds, an X–ray determination of the title compound (Fig. 1) was performed.

Experimental

The compound was provided by Tatsuo Sekiguchi of this laboratory. Purple needle-like crystals were obtained from a 1,2-dichloroethane solution. The cell dimensions and diffraction intensities were measured on a Rigaku AFC-4 four-circle diffractometer by using graphite-monochromated Mo $K\alpha$ radiation (λ=0.71069 Å) at room temperature. 1541 independent reflections with 2θ values up to 55° ($|F_o|\geq3\sigma(|F_o|)$) were used for the analysis. No correction was made for absorption.

Crystal Data: $C_{28}H_{28}N_2O_2$; M=424.54; monoclinic; space group $P2_1/c$; a=9.5115(4), b=15.712(1), c=15.174(1) Å, β=96.138(5)°; D_x=1.252 g cm^{-3} for Z=4. The structure was solved by the MULTAN 78 program.[2] The positions of the hydrogen atoms were obtained from the difference Fourier synthesis. The structural parameters were refined by the full-matrix least-squares method, using the UNICS III system.[3] Anisotropic thermal parameters were assumed for the non-hydrogen atoms, and isotropic parameters, for the hydrogen atoms. The final refinement, employing the weighting scheme of w=(0.012$|F_o|^2$−0.562$|F_o|$+7.949)$^{-1}$, led to the R value of 0.077. All the computations were carried out on a FACOM M-380 computer.

Results and Discussion

An ORTEP diagram[4] displaying the molecular structure is shown in Fig. 2. Table 1 lists the final atomic coordinates of the non-hydrogen atoms.[5]

The central four-membered ring (I) is planar within the limit of experimental error of 0.005 Å.
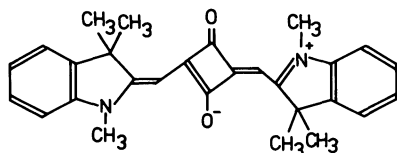

Fig. 1.   One of the resonance structures of the title compound.

The indoline rings (II and III) are planar within 0.03 Å and 0.06 Å respectively. The molecule is slightly folded at the C(3) atom and is twisted along the C(16)–C(17) bond. The II and III rings make angles of 7.8° and 24.6° respectively with the I ring. The molecule is roughly planar and adopts the trans conformation.

The bond lengths of C(2)-C(3), C(3)-C(4), C(16)-C(17), and C(17)-C(18) fall in the range of those of the conjugated C–C bonds. The shorter bond lengths of N(1)-C(4) and N(2)-C(18) compared with the corresponding bonds in N-thioacetylindoline[6] and 3-hydroxy-2,3-diphenylindoline[7] indicate that these

Table 1.   Fractional Atomic Coordinates($\times10^4$) and Equivalent Isotropic Thermal Parameters, with Estimated Standard Deviations in Parentheses

|	x	y	z	$B_{eq}/\text{Å}^2$
O(1)	7177(7)	228(3)	3803(4)	5.2(2)
O(2)	8537(7)	2049(4)	6043(4)	5.2(2)
N(1)	6360(7)	3484(4)	3057(4)	4.1(2)
N(2)	9090(7)	−1276(4)	6779(4)	4.0(2)
C(1)	7537(9)	713(5)	4421(6)	4.1(2)
C(2)	7584(8)	1633(5)	4494(5)	3.7(2)
C(3)	7065(9)	2204(5)	3824(6)	3.9(3)
C(4)	6998(9)	3078(5)	3779(5)	3.8(2)
C(5)	7544(9)	3739(5)	4463(5)	3.9(2)
C(6)	7157(9)	4559(5)	3972(5)	4.1(3)
C(7)	7372(9)	5396(6)	4241(6)	4.8(3)
C(8)	6855(12)	6036(6)	3652(7)	5.7(4)
C(9)	6110(13)	5825(6)	2843(8)	5.8(4)
C(10)	5899(11)	4999(6)	2585(6)	4.7(3)
C(11)	6434(9)	4373(5)	3153(5)	3.9(3)
C(12)	5737(16)	3091(8)	2242(7)	5.2(3)
C(13)	6803(13)	3699(7)	5308(7)	4.8(3)
C(14)	9134(11)	3662(7)	4694(8)	5.3(4)
C(15)	8165(9)	1567(5)	5433(6)	4.0(2)
C(16)	8139(8)	632(5)	5361(6)	3.8(2)
C(17)	8626(10)	53(5)	6012(6)	4.1(3)
C(18)	8471(8)	−810(5)	6095(5)	3.5(2)
C(19)	7502(8)	−1408(5)	5485(5)	3.7(2)
C(20)	7584(8)	−2210(5)	6025(5)	3.4(2)
C(21)	6899(9)	−2977(5)	5884(6)	4.2(3)
C(22)	7205(11)	−3621(6)	6492(6)	4.8(3)
C(23)	8155(11)	−3527(6)	7220(7)	5.1(3)
C(24)	8863(11)	−2768(6)	7372(6)	4.6(3)
C(25)	8545(8)	−2110(5)	6770(5)	3.7(2)
C(26)	10099(14)	−939(9)	7475(8)	5.4(3)
C(27)	6028(9)	−1067(6)	5284(6)	3.9(3)
C(28)	8202(11)	−1567(6)	4621(6)	4.0(3)
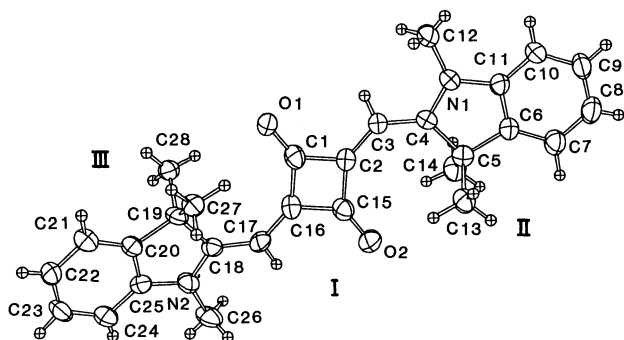
Fig. 2. Perspective view of the molecule showing the atom numbering scheme for the non-hydrogen atoms. Atoms are represented by thermal ellipsoids at 40% probability level. Hydrogen atoms are drawn at an arbitrarily small size. Selected bond lengths (l/Å) and angles (ϕ/°) are: C(2)–C(3) 1.404(12), C(3)–C(4) 1.377(12), C(16)–C(17) 1.385(12), C(17)–C(18) 1.372(12), N(1)–C(4) 1.353(11), N(2)–C(18) 1.353 (10), C(1)–C(2)–C(3) 125.1(8), C(3)–C(2)–C(15) 144.1(8), C(2)–C(4) 133.2(8), C(1)–C(16)–C(17) 143.8(8), C(15)–C(16)–C(17) 126.8(8), C(16)–C(17)– C(18) 133.1(8).
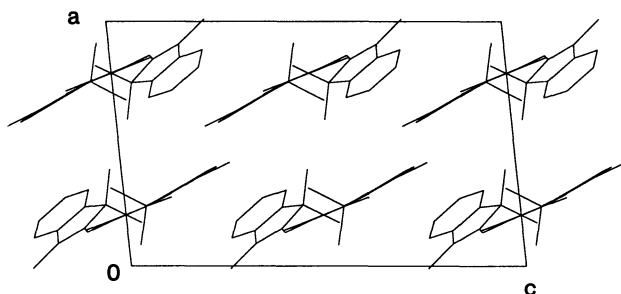

Fig. 3. Crystal structure projected along the b axis.

bonds are also involved in conjugation. The enlargement of the C(3)–C(2)–C(15), C(2)–C(3)–C(4),

C(1)–C(16)–C(17), and C(16)–C(17)–C(18) angles is due to the repulsive interactions between oxygen atoms and methyl carbons, C(13), C(14), C(27), and C(28). Such interactions are suggested by the short intramolecular distances of O(1)···C(27)=3.30(1), O(1)···C(28)=3.19(1), O(2)···C(13)=3.21(1), and O(2)···C(14)=3.34(1) Å.

The crystal structure is displayed in Fig. 3. Although several short intermolecular contacts are found (O(2)···C(24)=3.27(1), C(1)···C(27)=3.51(1), and C(15)···C(28)=3.46(1) Å), the molecules are held together by van der Waals forces. The twist of the III ring from the I ring probably results from the crystal packing.

References

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