References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Debaerdemaeker, T., Germain, G., Main, P., Refaat, L. S., Tate, C. & Woolfson, M. M. (1988). *MULTAN88. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Destro, R. & Marsh, R. E. (1987). *Acta Cryst.* A**43**, 711–718.

Dougherty, D. A. & Stauffer, D. A. (1990). *Science*, **250**, 1558–1560.

Duchamp, D. J. (1964). *CRYM Crystallographic Computing System.* Am. Crystallogr. Assoc. Meet., Bozeman, Montana, Paper B14, p. 29.

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.

Petti, M. A., Shepodd, T. J., Barrans, R. E. & Dougherty, D. A. (1988). *J. Am. Chem. Soc.* **110**, 6825–6840.

Stauffer, D. A. & Dougherty, D. A. (1988). *Tetrahedron Lett.* **29**, 6039–6042.

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Studies on Photochromism of a Thermally Stable Fulgide in the Crystalline State: X-ray Crystallographic Investigation of (*E*)-2-Isopropylidene-3-(1-naphthylmethylene)succinic Anhydride

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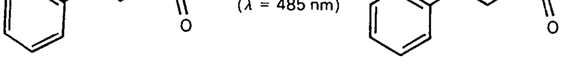
Abstract

(*E*)-2-Isopropylidene-3-(1-naphthylmethylene)succinic anhydride, $C_{18}H_{14}O_3$, $M_r = 278.31$, monoclinic, $P2_1/c$, $a = 13.408\ (1)$, $b = 8.762\ (1)$, $c = 13.431\ (1)$ Å, $\beta = 117.50\ (1)^\circ$, $V = 1399.5\ (3)$ Å^3, $Z = 4$, $D_m = 1.32$, $D_x = 1.321$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 0.69$ mm^{-1}, $F(000) = 584$, $T = 298$ K, $R = 0.057$ for 1777 observed reflections. The electrocyclic ring closure that the title compound undergoes in the solid state is viewed in terms of relevant geometrical parameters. The photochromism of the compound observed in the solid state appears to occur at defect sites, surfaces and microcavities.

Introduction

Interest in studies on photochromic compounds has been increasing ever since the potential applications of photochromic materials were realised in various areas such as the control and measurement of radiation intensity, optical computers and display systems (Brown, 1971; Dürr, 1989; Dürr & Bouas-Laurent, 1990). Among the very useful, as well as widely investigated, classes of photochromic compounds are fulgides (Dürr & Bouas-Laurent, 1990; Hanazawa, Sumiya, Horikawa & Irie, 1992; Suzuki, Tomoda, Ishizuka, Kaneko, Furui & Matsushima, 1989; Zhao, Ming, Zhu & Fan, 1992). Detailed investigations of several aspects including the mechanism, thermal stability, reusability and potential applications of a series of these compounds were carried out by Heller and co-workers (Heller & Megit, 1974; Hart, Heller, Megit & Szewczyk, 1975; Darcy, Heller, Strydom & Whittall, 1981; Heller & Langan, 1981; Heller, 1991). However, reports on the study of the mechanism of photochromism of these compounds in the solid state are relatively sparse. A report by Kaftory (1984) concerning the crystallographic study of a fulgide forms one example.

It was observed (Hart *et al.*, 1975) that irradiation of the yellow (*E*)-2-isopropylidene-3-(1-naphthylmethylene)succinic anhydride (I) at 366 nm in the crystalline state, in a rigid plastic matrix, and in benzene, produced a red coloration ($\lambda_{max} = 485$ nm) attributed to the formation of 4,4a-dihydrophenanthrene (DHP) (II). Upon exposure to white light, the colour change could be reversed, but did not occur in the dark. With the aim of gaining an insight into the structural aspects responsible for the observed phenomenon in the solid state, crystallographic analysis of the fulgide (I) has been carried out and the results are presented in this paper.



Yellow
(I)

Red
(II)

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Experimental

The title compound (I) was synthesized as reported by Hart *et al.* (1975). The spectral data and the m.p. were consistent with the reported values.

X-ray structural investigations

Good single crystals of (I), yellow in colour, were obtained by slow evaporation from a chloroform–ethanol (1:1) mixture. A crystal of size 0.4 × 0.2 × 0.2 mm and of good optical quality was chosen for data collection. Three-dimensional intensity data were obtained from an Enraf–Nonius CAD-4 diffractometer using nickel-filtered Cu $K\alpha$ (λ = 1.5418 Å) radiation in the ω–2θ mode; lattice parameters were determined by a least-squares fit of 25 accurately centred reflections in the range $10.8 \leq \theta \leq 39.1°$. A pre-scan speed of 5.5° min^{-1} was employed and the final scan was performed with a scan speed calculated to satisfy the condition, $\sigma(I)/I \leq 0.03$. The data were collected up to a maximum of $2\theta = 130°$ ($h = 0$ to 15, $k = 0$ to 10, $l = -15$ to 15). The stability and orientation of the crystal were monitored by measuring three standard reflections after every 3600 s of data collection; the orientation was checked after every 400 reflections and the fluctuations in these reflections ($1\bar{4}\bar{3}$, 113, 423) were below 2%. A total of 2257 unique reflections were measured of which 1777 were considered significant [$|F_o| > 3\sigma(F_o)$]. The data were corrected for Lorentz and polarization effects, but not for absorption.

The structure of (I) was determined by direct methods using *SHELXS*86 (Sheldrick, 1986). Full-matrix least-squares refinement, using *SHELX*76 (Sheldrick, 1976), of scale factor, positional and anisotropic thermal parameters of non-H atoms as well as positional and isotropic thermal parameters of the H atoms, all of which were located from a difference Fourier map (number of parameters = 246), converged to a final R value of 0.057, wR = 0.057 and S = 0.74. The function minimized was $\sum(w|F_o| - |F_c|)^2$ where $w = 1$. The maximum value of Δ/σ in the final refinement cycle was 0.001. The final difference Fourier map was essentially featureless with the maximum and minimum values being 0.16 and -0.19 e Å^{-3}, respectively. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Results and discussion

The atom numbering in (I) is depicted in Fig. 1 drawn using *ORTEP* (Johnson, 1976) and a stereopacking diagram obtained using *PLUTO* (Motherwell & Clegg, 1978) is presented in Fig. 2. The final positional parameters of the non-H atoms of (I) are listed in Table 1, relevant bond lengths and angles in Tables 2 and 3, respectively.*

It is known, from the work by Hart *et al.* (1975), that the conversion of (I) to (II) upon irradiation is as a result of an electrocyclic ring closure. Since it involves $4n + 2$ π electrons, the photochemical ring closure should, as per the principle of conservation of orbital symmetry (Woodward & Hoffmann, 1970), be a conrotatory process. As the reaction is known to occur in the crystalline state as well, it was considered worth examining whether relevant geometrical parameters obtained from the X-ray structure could permit a rationalization of the observed reaction.

The torsion angle about the C(5)—C(6) single bond *viz.* C(2)—C(5)—C(6)—C(7) is −49.3 (6)°, comparable to that observed (50°) by Kaftory (1984) in 2-isopropylidene-3-[1-(2-methyl-5-phenyl-3-thienyl)ethylidene]succinic anhydride (III). The π orbitals at the reactive centres in (I), C(7) and C(16), which should ideally be parallel to each other are in fact at an angle of *ca* 60° in the ground state, strikingly similar to the corresponding angle in (III), 58.8°. This geometry also appears to correspond to

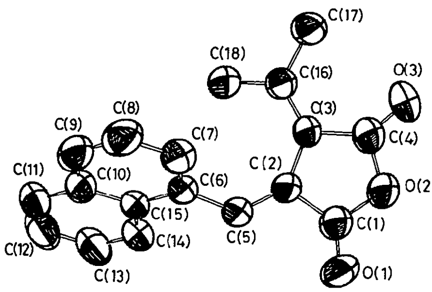

Fig. 1. *ORTEP* plot of a single molecule of compound (I) with the atomic numbering scheme.

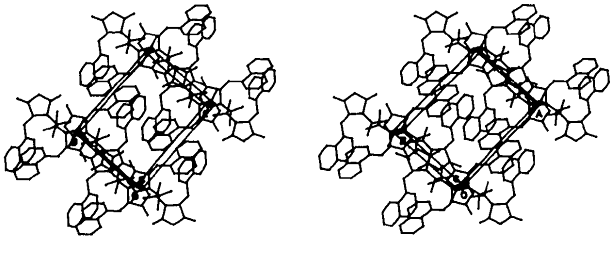

Fig. 2. Stereoview of the molecular packing of (I) viewed down the c axis.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71002 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0143]

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (× 10^4) *of the non*-H *atoms of* (I) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq} (Å^2)
O(1)	11229 (2)	3095 (3)	6931 (2)	884 (14)
O(2)	9727 (2)	1563 (3)	6249 (2)	740 (12)
O(3)	8555 (2)	− 422 (3)	5694 (3)	1054 (15)
C(1)	10874 (3)	1829 (4)	6776 (3)	649 (15)
C(2)	11465 (3)	345 (4)	7133 (3)	561 (15)
C(3)	10593 (2)	− 833 (4)	6630 (2)	544 (13)
C(4)	9505 (3)	− 15 (5)	6151 (3)	699 (17)
C(5)	12563 (3)	372 (4)	7857 (3)	621 (16)
C(6)	13309 (3)	− 849 (4)	8546 (3)	592 (16)
C(7)	12980 (3)	− 1745 (4)	9186 (3)	733 (20)
C(8)	13735 (4)	− 2830 (5)	9944 (3)	878 (22)
C(9)	14772 (4)	− 2997 (5)	10037 (4)	869 (23)
C(10)	15142 (3)	− 2134 (4)	9379 (3)	751 (17)
C(11)	16214 (4)	− 2317 (6)	9435 (4)	956 (23)
C(12)	16534 (4)	− 1493 (7)	8782 (5)	1074 (29)
C(13)	15800 (3)	− 397 (6)	8036 (4)	925 (24)
C(14)	14759 (3)	− 184 (5)	7962 (3)	750 (19)
C(15)	14390 (3)	− 1028 (4)	8628 (3)	603 (13)
C(16)	10667 (3)	− 2333 (4)	6416 (3)	580 (14)
C(17)	9670 (4)	− 3379 (5)	5931 (4)	739 (20)
C(18)	11740 (3)	− 3054 (5)	6613 (4)	733 (18)

Table 2. *Selected bond lengths* (Å) *involving non*-H *atoms with e.s.d.'s in parentheses*

O(1)—C(1)	1.187 (4)	C(7)—C(8)	1.419 (5)
O(2)—C(1)	1.384 (4)	C(8)—C(9)	1.345 (8)
O(2)—C(4)	1.408 (5)	C(9)—C(10)	1.415 (7)
O(3)—C(4)	1.185 (4)	C(10)—C(11)	1.413 (7)
C(1)—C(2)	1.482 (5)	C(10)—C(15)	1.426 (5)
C(2)—C(3)	1.469 (4)	C(11)—C(12)	1.350 (9)
C(2)—C(5)	1.338 (4)	C(12)—C(13)	1.408 (7)
C(3)—C(4)	1.479 (5)	C(13)—C(14)	1.365 (6)
C(3)—C(16)	1.359 (5)	C(14)—C(15)	1.414 (6)
C(5)—C(6)	1.465 (5)	C(16)—C(17)	1.499 (6)
C(6)—C(7)	1.378 (6)	C(16)—C(18)	1.479 (6)
C(6)—C(16)	1.411 (6)		

Table 3. *Selected bond angles* (°) *involving non*-H *atoms with e.s.d.'s in parentheses*

C(1)—O(2)—C(4)	110.5 (3)	C(6)—C(7)—C(8)	120.1 (4)
O(1)—C(1)—O(2)	120.5 (3)	C(7)—C(8)—C(9)	120.3 (4)
O(2)—C(1)—C(2)	108.6 (3)	C(8)—C(9)—C(10)	121.9 (4)
O(1)—C(1)—C(2)	130.7 (4)	C(9)—C(10)—C(15)	117.9 (4)
O(1)—C(2)—C(5)	117.6 (3)	C(9)—C(10)—C(11)	123.2 (4)
O(1)—C(2)—C(3)	105.9 (3)	C(11)—C(10)—C(15)	119.0 (4)
C(3)—C(2)—C(5)	136.1 (3)	C(10)—C(11)—C(12)	121.7 (5)
C(2)—C(3)—C(16)	131.0 (3)	C(11)—C(12)—C(13)	120.0 (5)
C(2)—C(3)—C(4)	106.0 (3)	C(12)—C(13)—C(14)	120.0 (5)
C(4)—C(3)—C(16)	122.0 (3)	C(13)—C(14)—C(15)	121.8 (4)
O(3)—C(4)—C(3)	133.4 (4)	C(10)—C(15)—C(14)	117.6 (4)
O(2)—C(4)—C(3)	108.2 (3)	C(6)—C(15)—C(14)	122.6 (4)
O(2)—C(4)—O(3)	118.3 (4)	C(6)—C(15)—C(10)	119.7 (4)
C(2)—C(5)—C(6)	130.3 (3)	C(3)—C(16)—C(18)	122.4 (3)
C(5)—C(6)—C(15)	120.5 (3)	C(3)—C(16)—C(17)	123.1 (4)
C(5)—C(6)—C(7)	119.2 (4)	C(17)—C(16)—C(18)	114.5 (3)
C(7)—C(6)—C(15)	120.1 (3)		

an isolated molecule of (I) as shown by molecular-mechanics calculations (*MMX* force field incorporated in the *PCMODEL* program; Serena Software, 1990). The value of the torsion angle about C(5)—C(6), after geometry optimization by the above method, is found to be −55.8°, and is not very different from that observed in the crystalline state, indicating that this is an inherent feature of the isolated molecule. The other torsion angles in (I) which are relevant are those involving the isopropylidene group, namely C(4)—C(3)—C(16)—C(17) [−15.5 (6)°] and C(4)—C(3)—C(16)—C(18) [162.6 (4)°]. Another important parameter to be taken into account is the distance between the reacting centres C(7)···C(16) which is 3.62 Å, and the corresponding value in (III) which is 3.9 Å.

The above geometrical parameters provide an estimate of the necessary rotation of portions of (I) about the C(5)—C(6) single bond, required to attain a transition state which would then undergo, upon irradiation, a conrotatory ring closure to give the product (II). However, the title compound is known to be weakly photochromic (Heller, 1990). To further ascertain the nature of the transformation, an X-ray powder diffraction study was undertaken. Firstly, the data of the finely powdered yellow fulgide, (I), were obtained in the 2θ range 0–45°, on a Stoe automatic powder diffractometer using Ge(111)-monochromatized Cu $K\alpha_1$ (λ = 1.5406 Å) radiation with a curved position-sensitive detector, and the diffractogram was recorded. The sample was then irradiated (λ = 366 nm) for 6 h during which time it turned orange in colour. Diffraction data of this sample were collected in similar fashion and the diffractogram obtained was strikingly similar to that of the sample before irradiation. The whole process was once again repeated after irradiation (λ = 366 nm) for 24 h and the resulting diffractogram did not exhibit any change in the postion of the peaks. Fig. 3 compares the patterns (in the 2θ range of 10.0–35.0°) of the sample after 0 and 6 h of UV exposure. The two patterns do not differ in the position of the peaks. Although there is a general decrease in the intensities of the peaks, presumably as a result of radiation decay, the ratios of the peaks relative to each other were similar in the irradiated and the unirradiated sample. This result suggests that the extent of the transformation is small. If the reaction were to take place in the bulk of the crystal,

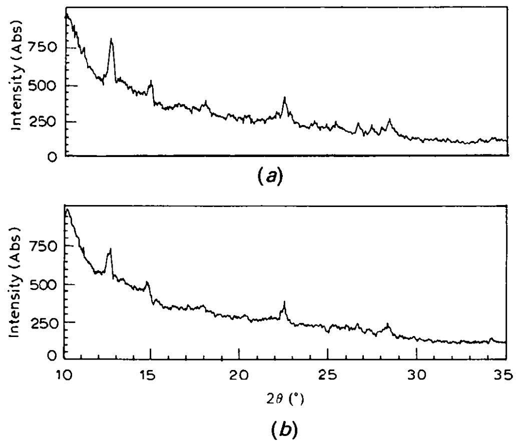

Fig. 3. Powder diffraction patterns of compound (I). (*a*) Before irradiation. (*b*) After 6 h of irradiation (λ = 366 nm).

there must be sufficient cavity volume available in the crystal lattice as the transformation requires large scale rotations of portions of the molecule about the C(5)—C(6) and C(3)—C(16) bonds. Whether or not the lattice allows such large-scale movements may easily be verified by lattice-energy calculations.

For the purpose of energy calculations the transformation (I) to (II) may be approximated to one consisting of two main geometric changes: (i) the torsion angle C(2)—C(5)—C(6)—C(7) which is −49.3° in (I) would decrease to about −5° in (II), (ii) the torsion angle C(2)—C(3)—C(16)—C(17) which is close to 180° in (I) would be about −90° in (II). The lattice-energy calculations were performed using the program *WMIN* (Busing, 1981). The energy was calculated by the pairwise van der Waals attractive and repulsive potential given below.

$$E = -\sum_{i}^{\text{one cell}} \sum_{j\neq i}^{\text{all cells}} A_iA_jr_{ij}^{-6} + \sum_{i}^{\text{one cell}} \sum_{j\neq i}^{\text{all cells}} D_iD_jr_{ij}^{-12}$$

The non-bonded interaction parameters used for lattice-energy calculations (A_i and D_i) are from Mirsky (1978). Contributions arising from the Coulombic interaction were not included.

The lattice energy of the fulgide (I) was computed to be −110.5 kJ mol^{-1}. The naphthyl group was then rotated in steps of 5° about the C(5)—C(6) bond until C(2)—C(5)—C(6)—C(7) reached a value of *ca* −5°. Simultaneously, for every 5° rotation of the naphthyl group, the atoms C(17) and C(18) were rotated about the C(3)=C(16) bond in such a way that when C(2)—C(5)—C(6)—C(7) reaches about −5°, the corresponding torsion angle C(2)—C(3)—C(16)—C(17) gets close to −90°. It is clear from Table 4 that as the magnitude of rotation increases the intermolecular interaction energy increases steeply. In these calculations the unit-cell dimensions and the space-group symmetry of the starting material (I) are kept unchanged. The results obtained coupled with the nature of the diffractograms suggest that the transformation (I) to (II) occurs not topochemically but rather at defect sites, microcavities and surfaces. The small yield of the product (II) observed by Heller *et al.* (1990) is noteworthy here.

Since molecule (I) is sterically overcrowded, the diene system is severely skewed, the torsion angle C(5)—C(2)—C(3)—C(16) being −27.0 (7)°. In (III), the corresponding torsion angle is 39 (1)°. Pasto & Scheidt (1975) have found a torsion angle of 52.3° in a slightly more sterically crowded diene system. The torsion angle C(1)—C(2)—C(3)—C(4) in (I), however, is much smaller, −8.9 (3)°, as a result of the rigidity of the succinic anhydride moiety. Severe steric interactions between the methyl group C(18) and the H atom H(7) of the naphthyl group appear to lead to the deviations in bond angles C(3)—C(2)—C(5) [136.2 (3)°] and C(2)—C(3)—C(16) [131.0 (3)°] from the normal values. The corresponding angles in (III) are 132.1 and 131.5°, respectively. A consequence of this angular distortion seems to be the development of a non-bonded interaction between the C(17) methyl group and the O atom O(3) of the carbonyl group. In the crystal structure of (I) two C—H···O-type intermolecular hydrogen-bonding interactions are observed: C(11)···O(3)′ $(x+1,\ -y-\frac{1}{2},\ z+\frac{1}{2})$ = 3.43 (1), H(11)···O(3)′ = 2.55 (5) Å and C(11)—H(11)···O(3)′ = 140 (3)°; C(17)···O(1)′$(-x+2,\ -y,\ -z+1)$ = 3.47 (1), H(171)···O(1)′ = 2.54 Å and C(17)—H(171)···O(1)′ = 155 (3)°.

Table 4. *Results of lattice-energy calculations*

Step No.	Rotation about C(5)—C(6) (°)	Rotation about C(3)=C(16) (°)	Energy (kJ mol^{-1})
1	—	—	−110.4
2	5	10	−79.9
3	10	20	−85.8
4	15	30	−64.0
5	20	40	−4.2
6	25	50	+209.2
7	30	60	+1029.3
8	35	70	+4725.4

To summarize, the relevant geometrical parameters obtained from the X-ray crystallographic analysis of (I), by and large, seem to be very close to those observed by Kaftory in (III), thereby adding to the generality of the geometric features of a thermally stable photochromic fulgide. It seems reasonable to conclude from the powder diffractograms as well as the lattice-energy calculations, that the observed reaction in the crystals of (I) occurs at defect sites and surfaces.

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References

Brown, G. H. (1971). *Photochromism, Techniques of Chemistry*, Vol. III. New York: Wiley–Interscience.

Busing, W. R. (1981). *WMIN*. Report ORNL-5747. Oak Ridge National Laboratory, Tennessee, USA.

Darcy, P. J., Heller, H. G., Strydom, P. J. & Whittall, J. (1981). *J. Chem. Soc. Perkin Trans.* 1, pp. 202–205.

Dürr, H. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 413–431.

Dürr, H. & Bouas-Laurent, H. (1990). *Photochromism: Molecules and Systems*. Amsterdam: Elsevier.

Hanazawa, M., Sumiya, R., Horikawa, Y. & Irie, M. (1992). *J. Chem. Soc. Chem. Commun.* pp. 206–207.

Hart, R. J., Heller, H. G., Megit, R. M. & Szewczyk, M. (1975). *J. Chem. Soc. Perkin Trans.* 1, pp. 2227–2232.

Heller, H. G. (1990). Personal communication.

Heller, H. G. (1991). *Electronic Materials: from Silicon to Organics*, edited by L. S. Miller & J. B. Mullin, pp. 471–483. New York: Plenum.

Heller, H. G. & Langan, J. R. (1981). *J. Chem. Soc. Perkin Trans.* 2, pp. 341–343.

Heller, H. G. & Megit, R. M. (1974). *J. Chem. Soc. Perkin Trans.* 1, pp. 923–927.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kaftory, M. (1984). *Acta Cryst.* C**40**, 1015 1019.

Mirsky, K. (1978). *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 169–182. Delft Univ. Press.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Pasto, D. J. & Scheidt, W. R. (1975). *J. Org. Chem.* **40**, 1444–1447.

Serena Software (1990). *PCMODEL* Molecular modelling software for IBM/XT/AT and compatibles. Serena Software, Bloomington, Indiana, USA.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Suzuki, H., Tomoda, A., Ishizuka, M., Kaneko, A., Furui, M. & Matsushima, R. (1989). *Bull. Chem. Soc. Jpn*, **62**, 3968–3971.

Woodward, R. B. & Hoffmann, R. (1970). *The Conservation of Orbital Symmetry*. New York: Academic Press.

Zhao, W., Ming, Y., Zhu, Z. & Fan, M. (1992). *J. Photochem. Photobiol. A*, pp. 235–240.

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Structural Studies of 'Push–Pull' Butadienes

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Abstract

Compound (I), ethyl 2-cyano-5-dimethylamino-3-methyl-2,4-pentadienoate, $C_{11}H_{16}N_2O_2$, $M_r = 208.26$, monoclinic, $P2_1/n$, $a = 7.679$ (2), $b = 13.368$ (2), $c = 11.756$ (2) Å, $\beta = 92.62$ (2)°, $V = 1205.5$ (4) Å^3, $Z = 4$, $D_x = 1.15$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 6.15$ cm^{-1}, $F(000) = 448$, $T = 293$ K, $R = 0.062$ for 1721 unique reflections. Compound (II), 4,4-bis(methylthio)-2-phenyl-1,3-butadiene-1,1-dicarbonitrile, $C_{14}H_{12}N_2S_2$, $M_r = 272.38$, triclinic, $P\bar{1}$, $a = 8.833$ (1), $b = 9.419$ (2), $c = 9.520$ (1) Å, $\alpha = 106.77$ (1), $\beta = 93.14$ (1), $\gamma = 109.61$ (1)°, $V = 704.2$ (2) Å^3, $Z = 2$, $D_x = 1.28$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 32.29$ cm^{-1}, $F(000) = 284$, $T = 293$ K, $R = 0.062$ for 2059 unique reflections. Compound (III), ethyl 2-cyano-5-dimethylamino-3-phenyl-2,4-pentadienoate, $C_{16}H_{18}N_2O_2$, $M_r = 270.33$, monoclinic, $C2/c$, $a = 17.468$ (1), $b = 13.753$ (4), $c = 15.218$ (1) Å, $\beta = 125.49$ (1)°, $V = 2976.7$ (9) Å^3, $Z = 8$, $D_x = 1.21$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 6.12$ cm^{-1}, $F(000) = 1152$, $T = 293$ K, $R = 0.055$ for 2211 unique reflections. Compound (IV), 4-dimethylamino-4-methylthio-3-phenyl-1,3-butadiene-1,1-dicarbonitrile, $C_{15}H_{15}N_3S$, $M_r = 269.36$, monoclinic, $P2_1/n$, $a = 9.951$ (1), $b = 10.040$ (1), $c = 14.764$ (2) Å, $\beta = 98.67$ (1)°, $V = 1458.9$ (2) Å^3, $Z = 4$, $D_x = 1.23$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 18.37$ cm^{-1}, $F(000) = 568$, $T = 293$ K, $R = 0.052$ for 2479 unique reflections. The influence of different electron donor–acceptor pairings on the molecular geometry is discussed.

Introduction

In recent years the need to discover organic materials with large quadratic nonlinear coefficients for application in optical signal processing has been recognized (Chemla & Zyss, 1987). Our earlier attempts to exploit 'push–pull' ethylenes as nonlinear optical materials showed that their second-harmonic generation efficiency was poor (Kanagapushpam, Padmanabhan & Venkatesan, 1987; Kanagapushpam & Venkatesan, 1987; Kanagapushpam, Venkatesan & Cameron, 1988; Dastidar, Guru Row & Venkatesan, 1991). The present investigation aims to examine the effects of substitution of donor–acceptor pairs on the π-electron system in 1,3-butadienes and the results obtained are expected to be relevant to reliable computation of molecular hyperpolarizability β *via* quantum-chemical methods.

The butadienes discussed in this paper are (I) ethyl 2-cyano-5-dimethylamino-3-methyl-2,4-pentadienoate, (II) 4,4-bis(methylthio)-2-phenyl-1,3-butadiene-1,1-dicarbonitrile, (III) ethyl 2-cyano-5-