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Structural Studies of 'Push–Pull' Butadienes

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Abstract

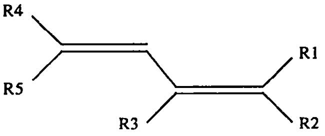
Compound (I), ethyl 2-cyano-5-dimethylamino-3-methyl-2,4-pentadienoate, $C_{11}H_{16}N_2O_2$, $M_r = 208.26$, monoclinic, $P2_1/n$, $a = 7.679$ (2), $b = 13.368$ (2), $c = 11.756$ (2) Å, $\beta = 92.62$ (2)°, $V = 1205.5$ (4) Å^3, $Z = 4$, $D_x = 1.15$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 6.15$ 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-

dimethylamino-3-phenyl-2,4-pentadienoate and (IV) 4-dimethylamino-4-methylthio-3-phenyl-1,3-butadiene-1,1-dicarbonitrile.



	(I)	(II)	(III)	(IV)
R1	COOEt	CN	COOEt	CN
R2	CN	CN	CN	CN
R3	CH_3	Ph	Ph	Ph
R4	NMe_2	SMe	NMe_2	SMe
R5	H	SMe	H	NMe_2

Experimental

All the compounds investigated were kindly provided by Dr M. Michalik, Zentral Institut für Organische Chemie, Rostock, Germany. Compounds (I) and (III) were crystallized from isopropanol and compounds (II) and (IV) from ethanol.

In all the cases, accurate cell dimensions and intensity data were obtained from an Enraf–Nonius CAD-4 diffractometer using monochromated Cu *Kα* ($\lambda = 1.5418$ Å) radiation in ω–2θ-scan mode. A prescan speed of 5.5° min^{-1} was employed and the final scan was performed with a scan speed calculated to satisfy the condition $\sigma(I)/I < 0.03$. The stability and orientation in all the cases were monitored by measuring three standard reflections after every 3600 s of data collection; the orientation was checked after every 400 reflections and no significant fluctuations in intensity were observed. The data were corrected for Lorentz and polarization effects, but not for absorption and extinction effects.

The structure of (I) was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). Isotropic refinement followed by anisotropic least-squares refinement of the non-H atoms converged to an *R* factor of 0.100. The atoms were located in a difference map at stereochemically reasonable positions. Full-matrix least-squares refinement, using *SHELX*76 (Sheldrick, 1976), of the scale factor, positional and anisotropic thermal parameters of the non-H atoms, and positional and isotropic thermal parameters of H atoms converged to $R = 0.062$ and $wR = 0.087$. The function minimized was $\sum(w|F_o| - |F_c|)^2$ where the weighting scheme used was $w = k/[\sigma^2(F_o) + g|F_c|^2]$ with $k = 1.0$ and $g = 0.014791$. There were no significant features in the difference Fourier map when the refinement was complete. The maximum and minimum values were 0.12 and -0.15 e Å^{-3}, respectively.

In the other three cases, structure solution and refinement were carried out as described for compound (I). Crystal data, data collection, methods of structure solution and refinement details for all four structures are summarized in Table 1.

Table 1. *Experimental data*

	(I)	(II)	(III)	(IV)
Crystal size (mm)	0.22 × 0.20 × 0.25	0.30 × 0.15 × 0.30	0.30 × 0.17 × 0.25	0.25 × 0.19 × 0.27
Number of centring reflections	25	25	25	25
θ range of centring reflections (°)	10–30	12–32	9–27	11–31
Range of *h* collected	0–8	0–9	0–19	0–11
Range of *k* collected	0–14	− 10–10	0–15	0–11
Range of *l* collected	− 14–14	− 10–10	− 17–17	− 17–17
Number of reflections collected	1969	2209	2976	2809
Number of unique reflections	1721	2059	2211	2479
$R_{\text{int}} = \sum(F - \langle F\rangle)/\sum F$	0.015	0.024	0.012	0.031
Number of observed reflections $[\lvert F_o\rvert > 3\sigma(F_o)]$	1335	1781	1605	1983
Method of structure solution	Direct methods	Direct methods	Direct methods	Direct methods
Number of variables	200	208	253	232
R value	0.062	0.062	0.055	0.052
wR	0.087	0.077	0.076	0.068
Weighting $w = k/[\sigma^2(F_o) + g\lvert F_o\rvert^2]$	$k = 1.0$; $g = 0.014$	$k = 1.0$; $g = 0.006$	$k = 1.0$; $g = 0.02$	$k = 1.0$; $g = 0.002$
S	0.94	1.16	0.75	1.34
Maximum residual difference density (e Å^{-3})	0.12	0.14	0.10	0.0008
Minimum residual difference density (e Å^{-3})	− 0.15	− 0.16	− 0.14	− 0.14

Results and discussion

Table 2 gives the final atomic parameters of the non-H atoms of compounds (I)–(IV).* Figs. 1–4 give *ORTEP*II (Johnson, 1976) plots of the molecules with numbering schemes. Figs. 5–8 show the molecular packing of all four butadienes using *PLUTO*82 (Motherwell, Sussman & Beebe, 1982). Table 3 records the intramolecular bond distances and angles. The shortening of the C(sp^2)—C(sp^2) and lengthening of the C=C bonds observed within the butadiene moiety in all four molecules when compared with the values reported for 1,3-butadiene [C=C = 1.337 (5) and C(sp^2)—C(sp^2) = 1.483 (1) Å] (Almenningen, Chemla, Bastiansen & Traetteberg, 1958) shows that these variations arise from the π-electron delocalization between the acceptors and donors *via* the butadiene moiety. The shortening of the C(sp^2)—N(sp^2) and C(sp^2)—S bond lengths highlights the partial double-bond character of these bonds. Examination of the C—S and C—N bond lengths in molecules (II) and (III) reveals that the

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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 71017 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0144]

Table 2. *Final atomic parameters involving non*-H *atoms for compounds* (I)–(IV) *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2 × 10^{-4})
(I)				
C(1)	−0.1536 (5)	0.2695 (3)	0.3503 (3)	679 (12)
C(2)	−0.0127 (5)	0.3366 (2)	0.3717 (3)	629 (11)
C(3)	−0.0348 (4)	0.4392 (2)	0.3489 (3)	591 (10)
C(4)	0.0994 (5)	0.5077 (3)	0.3617 (3)	655 (12)
C(5)	0.0766 (5)	0.6087 (3)	0.3454 (3)	615 (12)
C(6)	0.3805 (6)	0.6557 (4)	0.3859 (5)	940 (19)
C(7)	0.1521 (8)	0.7826 (3)	0.3442 (5)	845 (17)
C(8)	−0.2171 (6)	0.4722 (4)	0.3127 (5)	821 (16)
C(9)	0.1479 (5)	0.2923 (3)	0.4190 (3)	668 (13)
C(10)	0.2878 (6)	0.1401 (3)	0.4710 (6)	958 (22)
C(11)	0.2499 (8)	0.0320 (4)	0.4627 (7)	1146 (25)
N(1)	−0.2679 (5)	0.2150 (3)	0.3332 (3)	941 (15)
N(2)	0.1975 (4)	0.6778 (2)	0.3556 (2)	706 (11)
O(1)	0.2769 (4)	0.3356 (2)	0.4539 (3)	914 (11)
O(2)	0.1368 (3)	0.1923 (2)	0.4236 (2)	781 (10)
(II)				
C(1)	−0.1582 (4)	0.3281 (4)	0.5546 (4)	600 (14)
C(2)	−0.0608 (3)	0.2896 (3)	0.4436 (3)	494 (12)
C(3)	0.0828 (3)	0.2725 (3)	0.4812 (3)	461 (11)
C(4)	0.1439 (4)	0.3089 (4)	0.6341 (4)	543 (14)
C(5)	0.2548 (4)	0.2610 (4)	0.6933 (3)	533 (12)
C(6)	0.2018 (8)	0.4326 (7)	0.9672 (5)	937 (29)
C(7)	0.4572 (6)	0.0903 (7)	0.7180 (5)	788 (21)
C(8)	0.1706 (3)	0.2204 (4)	0.3609 (3)	475 (12)
C(9)	0.3251 (4)	0.3243 (5)	0.3593 (4)	627 (16)
C(10)	0.4116 (5)	0.2746 (7)	0.2492 (5)	820 (26)
C(11)	0.3461 (7)	0.1272 (8)	0.1463 (5)	886 (28)
C(12)	0.1918 (8)	0.0274 (7)	0.1448 (4)	905 (27)
C(13)	0.1023 (5)	0.0746 (4)	0.2531 (4)	684 (17)
C(14)	−0.1240 (4)	0.2751 (4)	0.2968 (4)	582 (14)
N(1)	−0.2328 (4)	0.3594 (4)	0.6449 (4)	810 (16)
N(2)	−0.1777 (5)	0.2645 (5)	0.1817 (4)	810 (17)
S(1)	0.3145 (1)	0.3157 (1)	0.8846 (1)	756 (6)
S(2)	0.3380 (1)	0.1314 (1)	0.5872 (1)	706 (5)
(III)				
C(1)	0.2768 (2)	−0.1448 (3)	0.8754 (3)	544 (19)
C(2)	0.3396 (2)	−0.0726 (2)	0.9529 (3)	510 (20)
C(3)	0.4279 (2)	−0.1010 (2)	1.0400 (2)	478 (18)
C(4)	0.4979 (3)	−0.0368 (2)	1.1163 (3)	538 (18)
C(5)	0.5852 (2)	−0.0671 (3)	1.2023 (3)	516 (20)
C(6)	0.7440 (3)	−0.0485 (4)	1.3644 (4)	708 (24)
C(7)	0.6406 (4)	−0.0941 (3)	1.2789 (4)	689 (28)
C(8)	0.4506 (2)	−0.2075 (2)	1.0536 (2)	467 (17)
C(9)	0.4126 (3)	−0.2674 (3)	1.0925 (3)	609 (22)
C(10)	0.4349 (3)	−0.3647 (3)	1.1097 (3)	722 (26)
C(11)	0.4936 (3)	−0.4041 (3)	1.0861 (4)	743 (23)
C(12)	0.5306 (3)	−0.3456 (3)	1.0463 (4)	761 (28)
C(13)	0.5089 (3)	−0.2468 (3)	1.0296 (3)	628 (22)
C(14)	0.3046 (3)	0.0268 (3)	0.9301 (3)	547 (20)
C(15)	0.1756 (4)	0.1302 (3)	0.8104 (5)	863 (33)
C(16)	0.1335 (6)	0.1531 (5)	0.8681 (8)	1106 (52)
O(1)	0.3454 (2)	0.0966 (2)	0.9868 (2)	702 (17)
O(2)	0.2178 (2)	0.0338 (2)	0.8374 (2)	747 (16)
N(1)	0.2283 (2)	−0.2034 (2)	0.8143 (3)	725 (19)
N(2)	0.6533 (2)	−0.0096 (2)	1.2769 (2)	577 (17)
(IV)				
C(1)	−0.0837 (3)	0.7301 (3)	0.0830 (2)	494 (9)
C(2)	−0.1014 (2)	0.5926 (3)	0.0992 (2)	434 (8)
C(3)	−0.0443 (2)	0.5372 (3)	0.1832 (2)	417 (7)
C(4)	0.0187 (3)	0.6203 (3)	0.2531 (2)	490 (9)
C(5)	0.0958 (3)	0.5814 (3)	0.3363 (2)	486 (9)
C(6)	−0.0397 (5)	0.7970 (5)	0.4034 (3)	819 (16)
C(7)	0.2269 (4)	0.4234 (5)	0.4401 (3)	758 (15)
C(8)	0.2368 (4)	0.4158 (5)	0.2739 (3)	738 (14)
C(9)	−0.0630 (2)	0.3922 (3)	0.1983 (2)	429 (8)
C(10)	−0.1082 (3)	0.3470 (3)	0.2771 (2)	533 (11)
C(11)	−0.1234 (4)	0.2126 (4)	0.2911 (3)	706 (12)
C(12)	−0.0942 (4)	0.1217 (4)	0.2264 (3)	742 (15)
C(13)	−0.0486 (4)	0.1648 (3)	0.1482 (2)	658 (12)
C(14)	−0.0339 (3)	0.2997 (3)	0.1340 (2)	539 (10)
C(15)	−0.1862 (3)	0.5218 (3)	0.0289 (2)	516 (9)
N(1)	−0.0676 (3)	0.8421 (3)	0.0728 (2)	678 (10)
N(2)	−0.2542 (3)	0.4694 (3)	−0.0298 (2)	744 (10)
N(3)	0.1766 (2)	0.4756 (2)	0.3489 (2)	544 (8)
S	0.0971 (1)	0.6822 (1)	0.4337 (1)	732 (3)

Table 3. *Bond distances* (Å) *and bond angles* (°) *involving non*-H *atoms for compounds* (I)–(IV)

(I)			
C(1)—C(2)	1.419 (5)	C(5)—N(2)	1.311 (4)
C(1)—N(1)	1.151 (5)	C(6)—N(2)	1.463 (5)
C(2)—C(3)	1.406 (3)	C(7)—N(2)	1.448 (5)
C(2)—C(9)	1.455 (5)	C(9)—O(1)	1.203 (4)
C(3)—C(4)	1.381 (4)	C(9)—O(2)	1.340 (4)
C(3)—C(8)	1.510 (5)	C(10)—C(11)	1.476 (6)
C(4)—C(5)	1.373 (5)	C(10)—O(2)	1.443 (5)
(II)			
C(1)—C(2)	1.440 (4)	C(6)—S(1)	1.773 (7)
C(1)—N(1)	1.142 (5)	C(7)—S(2)	1.793 (6)
C(2)—C(3)	1.372 (4)	C(8)—C(9)	1.391 (4)
C(2)—C(14)	1.427 (4)	C(8)—C(13)	1.366 (4)
C(3)—C(4)	1.424 (4)	C(9)—C(10)	1.395 (6)
C(3)—C(8)	1.477 (4)	C(10)—C(11)	1.354 (7)
C(4)—C(5)	1.365 (5)	C(11)—C(12)	1.368 (8)
C(5)—S(1)	1.741 (2)	C(12)—C(13)	1.395 (7)
C(5)—S(2)	1.738 (3)	C(14)—N(2)	1.133 (5)
(III)			
C(1)—C(2)	1.441 (4)	C(8)—C(9)	1.387 (6)
C(1)—N(1)	1.147 (4)	C(8)—C(13)	1.376 (7)
C(2)—C(3)	1.383 (3)	C(9)—C(10)	1.375 (5)
C(2)—C(14)	1.454 (5)	C(10)—C(11)	1.379 (8)
C(3)—C(4)	1.405 (3)	C(11)—C(12)	1.373 (8)
C(3)—C(8)	1.500 (3)	C(12)—C(13)	1.393 (5)
C(4)—C(5)	1.376 (4)	C(14)—O(1)	1.208 (4)
C(5)—N(2)	1.327 (4)	C(14)—O(2)	1.347 (3)
C(6)—N(2)	1.456 (4)	C(15)—C(16)	1.470 (16)
C(7)—N(2)	1.446 (5)	C(15)—O(2)	1.455 (5)
(IV)			
C(1)—C(2)	1.416 (4)	C(6)—S	1.788 (5)
C(1)—N(1)	1.148 (4)	C(7)—N(3)	1.461 (5)
C(2)—C(3)	1.399 (3)	C(8)—N(3)	1.464 (5)
C(2)—C(15)	1.425 (3)	C(9)—C(10)	1.385 (4)
C(3)—C(4)	1.399 (4)	C(9)—C(14)	1.389 (4)
C(3)—C(9)	1.488 (4)	C(10)—C(11)	1.376 (5)
C(4)—C(5)	1.402 (3)	C(11)—C(12)	1.383 (6)
C(5)—N(3)	1.328 (3)	C(12)—C(13)	1.372 (5)
C(5)—S	1.756 (3)	C(13)—C(14)	1.381 (4)
		C(15)—N(2)	1.144 (4)
(I)			
C(2)—C(1)—N(1)	179.8 (3)	C(4)—C(5)—N(2)	126.4 (3)
C(1)—C(2)—C(9)	115.8 (3)	C(2)—C(9)—O(2)	111.5 (3)
C(1)—C(2)—C(3)	119.8 (3)	C(2)—C(9)—O(1)	127.2 (3)
C(3)—C(2)—C(9)	124.2 (2)	O(1)—C(9)—O(2)	121.2 (3)
C(2)—C(3)—C(8)	116.1 (3)	C(11)—C(10)—O(2)	107.1 (3)
C(2)—C(3)—C(4)	122.8 (3)	C(6)—N(2)—C(7)	116.2 (3)
C(4)—C(3)—C(8)	120.9 (3)	C(5)—N(2)—C(7)	120.4 (3)
C(3)—C(4)—C(5)	123.1 (3)	C(5)—N(2)—C(6)	123.2 (3)
		C(9)—O(2)—C(10)	116.5 (3)
(II)			
C(2)—C(1)—N(1)	178.5 (4)	C(3)—C(8)—C(9)	118.2 (2)
C(1)—C(2)—C(14)	114.8 (2)	C(9)—C(8)—C(13)	120.5 (3)

Table 3 (*cont.*)

C(1)—C(2)—C(3)	120.9 (2)	C(3)—C(8)—C(13)	121.2 (3)
C(3)—C(2)—C(14)	124.2 (2)	C(8)—C(9)—C(10)	118.8 (3)
C(2)—C(3)—C(8)	118.4 (2)	C(9)—C(10)—C(11)	120.3 (5)
C(2)—C(3)—C(4)	119.2 (2)	C(10)—C(11)—C(12)	120.6 (4)
C(4)—C(3)—C(8)	122.3 (2)	C(11)—C(12)—C(13)	120.0 (4)
C(3)—C(4)—C(5)	128.1 (3)	C(8)—C(13)—C(12)	119.4 (4)
C(4)—C(5)—S(2)	123.5 (2)	C(2)—C(14)—N(2)	178.1 (4)
C(4)—C(5)—S(1)	122.0 (2)	C(5)—S(1)—C(6)	105.6 (2)
S(1)—C(5)—S(2)	114.2 (1)	C(5)—S(2)—C(7)	105.8 (1)
(III)			
C(2)—C(1)—N(1)	178.6 (4)	C(8)—C(9)—C(10)	120.3 (4)
C(1)—C(2)—C(14)	115.9 (3)	C(9)—C(10)—C(11)	120.2 (4)
C(1)—C(2)—C(3)	119.0 (2)	C(10)—C(11)—C(12)	119.7 (4)
C(3)—C(2)—C(14)	125.0 (3)	C(11)—C(12)—C(13)	120.2 (5)
C(2)—C(3)—C(8)	117.7 (2)	C(8)—C(13)—C(12)	119.9 (4)
C(2)—C(3)—C(4)	124.4 (2)	C(2)—C(14)—O(2)	112.2 (3)
C(4)—C(3)—C(8)	117.7 (2)	C(2)—C(14)—O(1)	125.7 (3)
C(3)—C(4)—C(5)	123.2 (3)	O(1)—C(14)—O(2)	121.9 (3)
C(4)—C(5)—N(2)	125.5 (3)	C(16)—C(15)—O(2)	111.9 (5)
C(3)—C(8)—C(13)	121.5 (3)	C(14)—O(2)—C(15)	116.0 (3)
C(3)—C(8)—C(9)	119.0 (3)	C(6)—N(2)—C(7)	116.2 (3)
C(9)—C(8)—C(13)	119.4 (3)	C(5)—N(2)—C(7)	122.2 (3)
		C(5)—N(2)—C(6)	121.5 (3)
(IV)			
C(2)—C(1)—N(1)	177.7 (3)	C(3)—C(9)—C(10)	120.6 (2)
C(1)—C(2)—C(15)	115.9 (2)	C(10)—C(9)—C(14)	118.8 (2)
C(1)—C(2)—C(3)	119.5 (2)	C(9)—C(10)—C(11)	120.2 (3)
C(3)—C(2)—C(15)	124.3 (2)	C(10)—C(11)—C(12)	120.2 (3)
C(2)—C(3)—C(9)	118.5 (2)	C(11)—C(12)—C(13)	120.2 (3)
C(2)—C(3)—C(4)	119.5 (2)	C(12)—C(13)—C(14)	119.5 (3)
C(4)—C(3)—C(9)	121.6 (2)	C(9)—C(14)—C(13)	120.9 (2)
C(3)—C(4)—C(5)	127.2 (2)	C(2)—C(15)—N(2)	177.2 (3)
C(4)—C(5)—S	119.4 (2)	C(7)—N(3)—C(8)	115.3 (2)
C(4)—C(5)—N(3)	125.8 (2)	C(5)—N(3)—C(8)	121.9 (2)
N(3)—C(5)—S	114.6 (2)	C(5)—N(3)—C(7)	122.1 (2)
C(3)—C(9)—C(14)	120.5 (2)	C(5)—S—C(6)	104.7 (1)

double-bond character of the C—N bond is much greater than that of the C—S bond showing that the electron-donating capacity of the NMe_2 group is greater than that of SMe. Also it may be noted that the bond-length variation in molecule (IV) shows greater delocalization than in (II) indicating that the donor–acceptor pairing in (IV) is better than in (II).

Molecules (I) and (III) are essentially planar as seen from their torsion angles. On the whole, the replacement of a methyl group in (I) by a phenyl group in (III) has not resulted in a significant difference in the molecular geometry between these molecules.

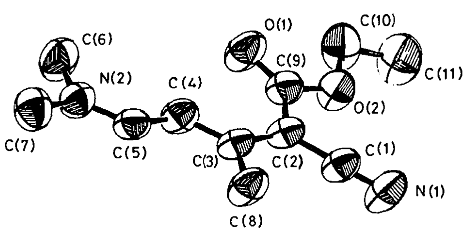

Fig. 1. *ORTEP* drawing of (I) with numbering scheme; non-H atoms are drawn as primary ellipses at the 50% probability level.

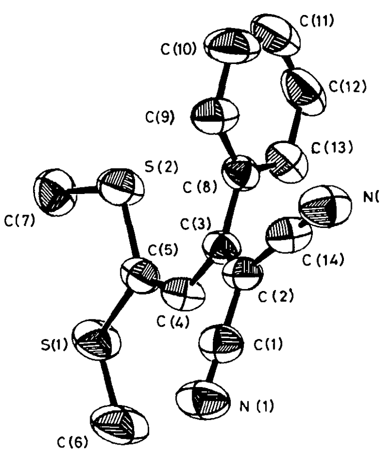

Fig. 2. *ORTEP*II drawing of (II) with numbering scheme; non-H atoms are drawn as primary ellipses at the 50% probability level.

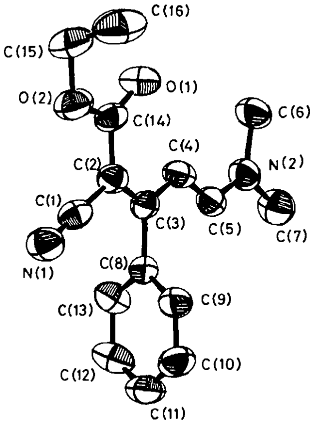

Fig. 3. *ORTEP*II drawing of (III) with numbering scheme; non-H atoms are drawn as primary ellipses at the 50% probability level.

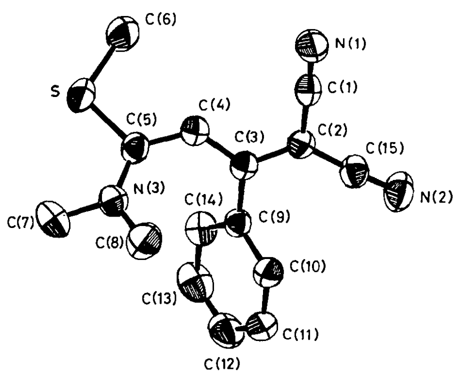

Fig. 4. *ORTEP*II drawing of (IV) with numbering scheme; non-H atoms are drawn as primary ellipses at the 50% probability level.

The butadiene moieties in both molecule (II) and molecule (IV) are by no means planar (see Table 4). The torsion angle C(2)—C(3)—C(4)—C(5) in (II) is 160.4 (3)°. The deviation of atom C(5) from the plane through S(1), S(2) and C(4) is as large as −0.172 (4) Å. In molecule (IV), the butadiene moiety is more planar than in (II), although there are deviations of the order of ± 0.045 Å. The deviations of the donor-group atoms N(3) and S suggest that there must be significant rotation about the C(4)═C(5) bond. In fact the values of the torsion angles C(3)—C(4)═C(5)—S and C(3)—C(4)═C(5)—N(3) are −149.3 (2) and 34.3 (5)°, respectively. Further the N(3) atom shows significant pyramidality, with a deviation of 0.061 (1) Å from the atoms bonded to it whereas the C(5) atom lies off the plane through S, N(3) and C(4) by about −0.027 (3) Å. However, on the acceptor side, the rotation about C(2)═C(3) bond [C(1)—C(2)—C(3)—C(4) = 5.8 (4), C(4)—C(3)—C(2)—C(15) = −169.5 (2)°] is not large and the deviation of atom C(2) from the plane through C(3), C(1) and C(15) is 0.039 (2) Å.

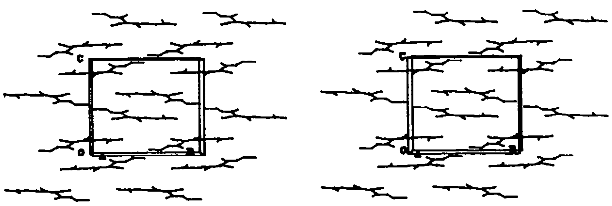

Fig. 5. *PLUTO* packing diagram of (I) viewed down the *a* axis.

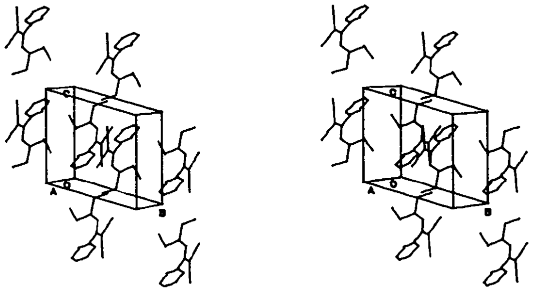

Fig. 6. *PLUTO* packing diagram of (II) viewed down the *a* axis.

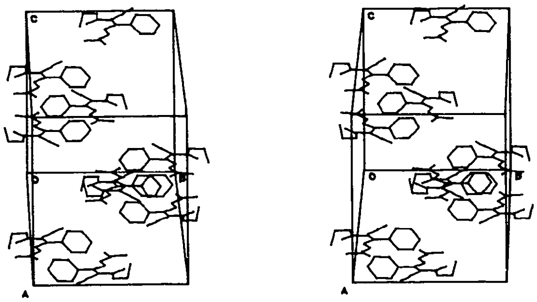

Fig. 7. *PLUTO* packing diagram of (III) viewed down the *a* axis.

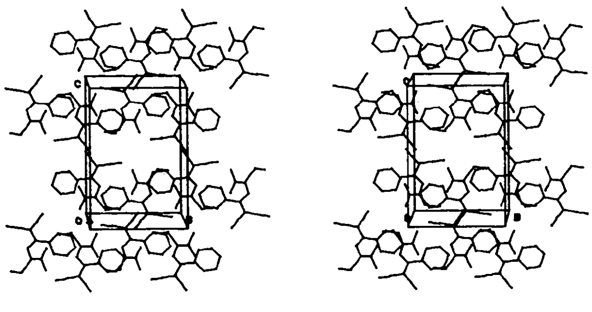

Fig. 8. *PLUTO* packing diagram of (IV) viewed down the *a* axis.

Table 4. *Selective least-squares planes for compounds* (II) *and* (IV)

	Least-squares plane	Deviation of atoms from the LS plane (Å)	
(II)	C(2), C(3), C(4), C(5)	C(2)	0.065 (1)
		C(3)	−0.049 (1)
		C(4)	−0.162 (1)
		C(5)	0.075 (1)
		C(1)	0.206 (3)
		S(1)	−0.099 (1)
		S(2)	0.678 (1)
		C(14)	0.026 (1)
(IV)	C(2), C(3), C(4), C(5)	C(2)	0.042 (1)
		C(3)	−0.035 (1)
		C(4)	−0.053 (1)
		C(5)	0.046 (1)
		C(1)	0.226 (3)
		C(15)	−0.145 (3)
		N(3)	0.768 (1)
		S	−0.761 (1)

Since the molecular modes of packing (Figs. 5–8) of these crystals are dictated only by weak van der Waals intermolecular interactions, the features of the molecular geometry observed in all cases may be assumed to be characteristic of the isolated molecules and hence would be valuable in the theoretical estimation of second-order hyperpolarizability β.

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Crystal Structure Correlations in the Photochemistry of Dimethyl 9-Chloromethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

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Abstract

A study of the photochemistry of the title 9-chloromethyldibenzobarrelene-11,12-diester (1) reveals the formation of semibullvalene derivatives [(2) and (3)] in acetone solution, with additional novel photoproducts [two isomers of dimethyl 5-chloro-10-methylene-5,5a,10,10a-tetrahydroindeno[2,1-*a*]indene-5a,10a-dicarboxylate; (4) and (5)] in other solvents, and especially in solid-state photolysis. The structures of (1), (4) and (5) have been determined by X-ray crystal analyses. Crystal data: $T = 294$ K, Cu $K\alpha$, $\lambda = 1.5418$ Å, $C_{21}H_{17}ClO_4$, $M_r = 368.82$. (1), monoclinic, $P2_1/c$, $a = 10.087$ (1), $b = 16.207$ (1), $c = 11.233$ (1) Å, $\beta = 107.64$ (1)°, $V = 1749.9$ (2) Å^3, $Z = 4$, $D_x = 1.400$ g cm^{-3}, $F(000) = 768$, $\mu = 21.4$ cm^{-1}, $R = 0.042$ for 2569 reflections. (4), triclinic, $P\bar{1}$, $a = 13.893(1)$, $b = 15.968$ (2), $c = 8.191$ (2) Å, $\alpha = 98.13$ (2), $\beta = 91.78$ (2), $\gamma = 99.54$ (1)°, $V = 1771.2$ (4) Å^3, $Z = 4$ (two molecules per asymmetric unit), $D_x = 1.383$ g cm^{-3}, $\mu = 21.2$ cm^{-1}, $R = 0.045$ for 5645 reflections. (5) [15% (4) as impurity], monoclinic, $P2_1/c$, $a = 14.777$ (1), $b = 8.581$ (1), $c = 15.192$ (1) Å, $\beta = 112.10$ (1)°, $V = 1784.8$ (3) Å^3, $Z = 4$, $D_x = 1.372$ g cm^{-3}, $F(000) = 768$, $\mu = 21.0$ cm^{-1}, $R = 0.103$ for 2874 reflections. Photolysis of (1) in acetone results in the formation, *via* the triplet excited state, of the normal di-π-methane photoproducts (2) and (3). In other solvents and in the solid state, photolysis, *via* the singlet excited state, results in the novel dibenzopentalenes, (4) and (5); the mechanism by which these products are formed probably involves photorearrangement *via* a biradical (6), followed by a non-concerted Cl-atom migration. Solid-state photolysis produces relatively larger amounts of (4) and (5), and this information may be correlated with a favorable intermolecular C···Cl contact of 4.28 Å in the crystal structure of (1).

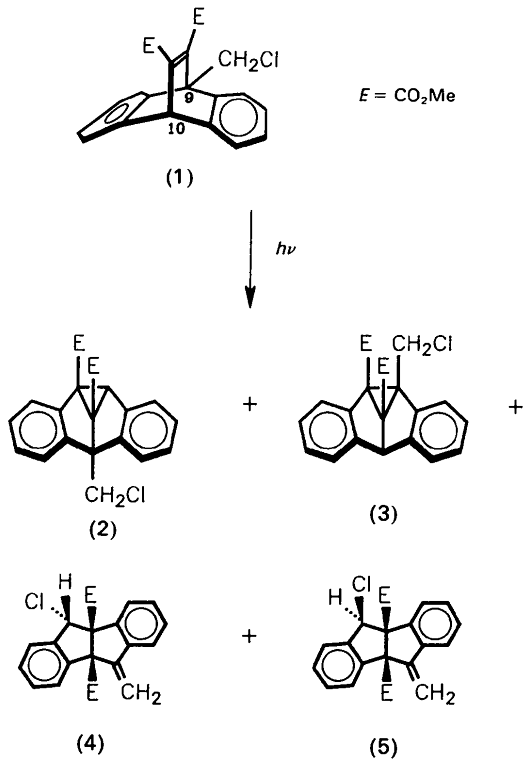

Fig. 1. Photolysis of compound (1).

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