

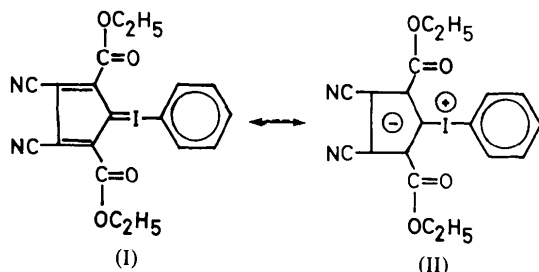
## The Structure of Phenyliodonio-2,5-diethoxycarbonyl-3,4-dicyanocyclopentadienide

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**Abstract.**  $C_{19}H_{15}IN_2O_4$ ,  $M_r = 462.24$ , monoclinic,  $P2/c$ ,  $Z = 4$ ,  $a = 13.558$  (8),  $b = 9.587$  (4),  $c = 15.882$  (8) Å,  $\beta = 113.95$  (4)°,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 17.2988$  cm<sup>-1</sup>,  $V = 1886.61$  Å<sup>3</sup>,  $D_m = 1.62$ ,  $D_c = 1.63$  g cm<sup>-3</sup>,  $F(000) = 912$ . The structure has been determined by Patterson and Fourier techniques and refined by least-squares analysis to an  $R$  value of 0.056 for 2801 reflexions. Compensation of the positive charge of the iodonium atom is intramolecular and the molecules in the unit cell are attracted by van der Waals forces.



**Introduction.** Friedrich & Amann (1973) succeeded in synthesizing the first stable iodonium ylide of the cyclopentadienyl anion. To answer the question which of the two possible mesomeric forms [(I) or (II)] these substances prefer, the most stable ylide, phenyl-iodonio-2,5-diethoxycarbonyl-3,4-dicyanocyclopentadienide, of this series was submitted to an X-ray structure analysis.

Because this ylide only crystallizes in a double-twinned form, suitable single crystals were very difficult to obtain. Mechanical cleaving of big twinned specimens solved this problem. Precise lattice parameters were obtained by least-squares fitting of the powder pattern.

X-ray intensities were measured on an automatic Nonius CAD-4 diffractometer, with graphite-monochromated Mo  $K\alpha$  radiation and pulse-height discrimination. A single crystal with dimensions  $0.4 \times 0.04 \times 0.04$  mm was used for collecting the intensities of 4183 independent reflexions ( $1.7 < \theta < 31^\circ$ ) in the  $\omega$ - $2\theta$  scan mode. Of these, 2801 were considered as 'observed' according to the criterion  $I > 2\sigma(I)$  and used for the refinement step. Two reflexions were monitored

periodically during the data collection and showed no crystal decomposition. The intensities were corrected for absorption.

The structure was solved with Patterson and Fourier techniques. The carbon atoms of the benzene ring were difficult to locate. This can be seen in the large standard deviations of these atoms. Structure factors calculated with the coordinates of the last Fourier synthesis and an assumed overall temperature factor of  $5.2 \text{ \AA}^2$  gave a discrepancy index  $R = 0.17$ . Scattering factors for neutral C, O, N, H and I (with  $f' = -0.6$  and  $f'' = 2.17$ ) were taken from Hanson, Herman, Lea & Skillman (1964).

After four cycles of full-matrix isotropic refinement for the 2801 observed reflexions and six more cycles with anisotropic temperature factors (blocked refinement), the conventional  $R$  index was 0.064. A difference synthesis calculated with those observed reflexions with  $\sin \theta/\lambda < 0.5 \text{ \AA}^{-1}$  located 70% of the H atoms. The remaining H atoms appeared as rather broad maxima in the synthesis.

An appropriate weighting scheme for the refinement was  $w = w_1 w_2$ , where  $w_1 = 1/\sigma_1^2$  and  $w_2 = 1/\sigma_2^2$  with  $\sigma_1 = a + b|F_o|$  and  $\sigma_2 = c + d(\sin \theta/\lambda) + e(\sin \theta/\lambda)^2$  (coefficients given in Table 1), calculated by the program *PESOS* (Martinez-Ripoll & Cano, 1975). All H atoms were placed at the expected positions with the program *HSEARCH* (Fayos & Martinez-Ripoll, 1975). After six cycles of blocked least-squares refinement assuming isotropic temperature factors for the H atoms and keeping some H positions fixed, the final unweighted and weighted disagreement factors were  $R = 0.056$  and  $R_w = 0.063$ . The fractional coordinates are given in Table 2.†

**Discussion.** Fig. 1 shows the shape of the molecule in the crystal, Table 3 gives the bond lengths and Table 4 the bond angles of the molecule. The atoms of the benzene and of the cyclopentadienyl rings lie in planes without significant deviations (see Table 5). The angle between both planes is  $82^\circ$ .

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33628 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Coefficients of the weighting scheme*

$ F_o $ (min)	$ F_o $ (max)	<i>a</i>	<i>b</i>		
1.00	3.02	2.3888	0.4061		
3.02	8.85	3.7308	-0.0757		
8.85	318.00	2.5566	-0.0495		
$\sin \theta/\lambda$ (min)	$\sin \theta/\lambda$ (max)	<i>c</i>	<i>d</i>	<i>e</i>	
0.04 Å <sup>-1</sup>	0.72 Å <sup>-1</sup>	3.7854	-13.4465	14.5588	

 Table 2. *Fractional atomic coordinates of heavy atoms ( $\times 10^5$ ) and hydrogen atoms ( $\times 10^3$ ) with standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	77427 (47)	43461 (57)	76225 (51)
C(2)	80418 (76)	39424 (75)	69265 (73)
C(3)	74056 (106)	42883 (116)	60424 (79)
C(4)	64908 (107)	50631 (133)	58667 (85)
C(5)	61967 (65)	54801 (88)	65733 (91)
C(6)	68317 (53)	51294 (70)	74764 (62)
C(7)	83839 (45)	16900 (51)	89122 (47)
C(8)	90729 (45)	6126 (54)	88863 (47)
C(9)	95600 (43)	-6774 (55)	89228 (46)
C(10)	75567 (47)	-3366 (55)	89632 (49)
C(11)	74533 (45)	11345 (57)	89558 (50)
C(12)	100931 (48)	7502 (60)	87948 (52)
C(13)	114904 (56)	-4946 (91)	85899 (64)
C(14)	117454 (81)	-20022 (107)	85112 (78)
C(15)	65279 (49)	19228 (68)	89745 (56)
C(16)	47924 (80)	17617 (118)	89271 (124)
C(17)	39562 (83)	7376 (174)	86423 (122)
C(18)	89478 (44)	-20382 (54)	89691 (48)
C(19)	68243 (52)	-13866 (66)	89885 (59)
N(1)	92384 (53)	-31748 (52)	90319 (53)
N(2)	62783 (60)	-22615 (70)	90171 (68)
O(1)	105290 (47)	18423 (51)	87734 (55)
O(2)	104938 (36)	-4827 (46)	87206 (40)
O(3)	64678 (47)	31725 (52)	89378 (52)
O(4)	57892 (46)	10937 (56)	90078 (67)
I	87555 (2)	38007 (3)	89723 (3)
H(1)	871 (10)	346 (14)	715 (9)
H(2)	753 (12)	393 (14)	553 (10)
H(3)	616 (9)	525 (12)	519 (8)
H(4)	552 (0)	603 (0)	642 (0)
H(5)	676 (5)	542 (7)	808 (4)
H(6)	1140 (6)	1 (8)	800 (5)
H(7)	1208 (7)	-8 (9)	914 (6)
H(8)	1122 (7)	-241 (9)	794 (6)
H(9)	1189 (11)	-240 (14)	914 (9)
H(10)	1248 (11)	-181 (15)	843 (9)
H(11)	494 (12)	200 (16)	952 (10)
H(12)	457 (12)	266 (16)	854 (10)
H(13)	414 (0)	-9 (0)	907 (0)
H(14)	387 (0)	34 (0)	801 (0)
H(15)	327 (0)	117 (0)	858 (0)

The bond lengths and angles in the benzene ring are slightly distorted. As Atwood & Sheppard (1975) found a similar distortion in the 4,5-dicyano-2-imidazolyl(phenyl)bromonium ylide, this could be characteristic of ylides. Trefonas & Majeste (1965) however correlate such distortions with the high electron density of the I atom.

The similar bond lengths in the cyclopentadienyl ring together with the planarity of the ring are due to its aromaticity and are comparable with other  $\pi$ -cyclopentadienyls (Churchill & Kalra, 1973).

The bond lengths C(1)—I and C(7)—I are nearly the same, the bond angle is 98.65°. The two torsion angles C(6)—C(1)—I—C(7) and C(1)—I—C(7)—C(8) are 107.84 and 106.89° (Shmueli, 1974). This similarity of bond lengths together with the planarity of the cyclopentadienyl ring gives proof of the mesomeric form (II).

The loose packing of the molecules in the unit cell, which can be seen in Fig. 2, seems to contradict the polar form (II) which should prefer closer packing with the possibility of intermolecular charge compensation.

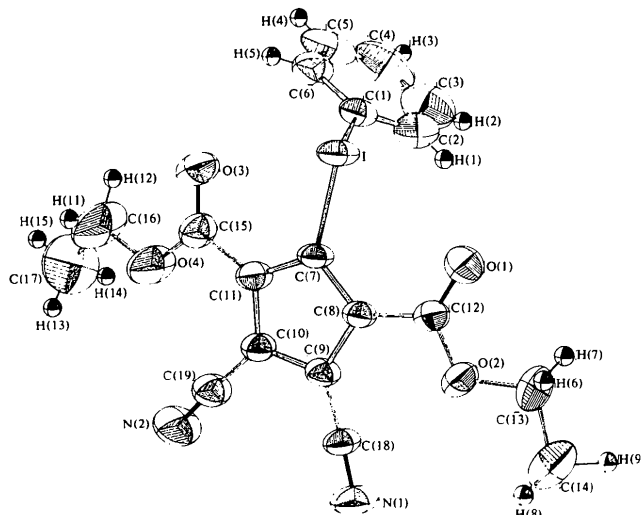


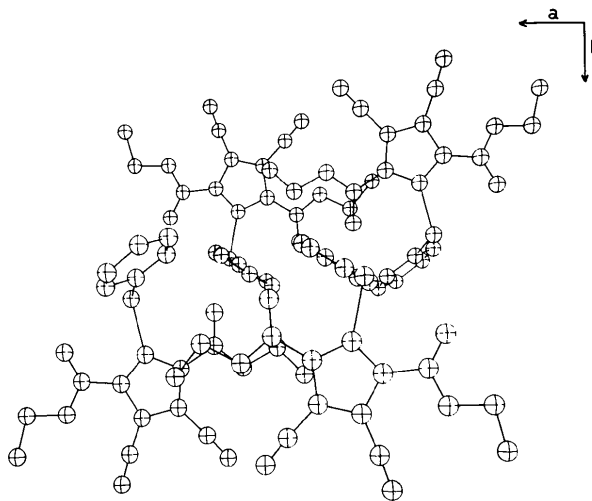
Fig. 1. The molecular structure of phenyliodonio-2,5-diethoxycarbonyl-3,4-dicyanocyclopentadienide.

 Table 3. *Bond lengths (Å) with standard deviations in parentheses*

I—C(1)	2.089 (7)	C(12)—O(2)	1.326 (8)
I—C(7)	2.078 (5)	C(15)—O(4)	1.296 (10)
C(1)—C(2)	1.378 (15)	O(2)—C(13)	1.448 (11)
C(2)—C(3)	1.357 (14)	O(4)—C(16)	1.453 (14)
C(3)—C(4)	1.374 (19)	C(13)—C(14)	1.503 (14)
C(4)—C(5)	1.393 (22)	C(16)—C(17)	1.427 (17)
C(5)—C(6)	1.382 (14)	C(2)—H(1)	0.952 (136)
C(6)—C(1)	1.382 (10)	C(3)—H(2)	0.964 (180)
C(7)—C(8)	1.404 (9)	C(4)—H(3)	0.994 (118)
C(8)—C(9)	1.431 (8)	C(5)—H(4)	1.003 (25)
C(9)—C(10)	1.426 (10)	C(6)—H(5)	1.051 (86)
C(10)—C(11)	1.417 (8)	C(13)—H(6)	1.013 (87)
C(11)—C(7)	1.397 (10)	C(13)—H(7)	0.997 (81)
C(8)—C(12)	1.454 (11)	C(14)—H(8)	0.977 (85)
C(11)—C(15)	1.475 (10)	C(14)—H(9)	1.006 (153)
C(9)—C(18)	1.397 (8)	C(14)—H(10)	1.076 (171)
C(10)—C(19)	1.426 (10)	C(16)—H(11)	0.903 (168)
C(18)—N(1)	1.149 (7)	C(16)—H(12)	1.031 (159)
C(19)—N(2)	1.132 (11)	C(17)—H(13)	1.012 (17)
C(12)—O(1)	1.210 (9)	C(17)—H(14)	1.037 (19)
C(15)—O(3)	1.201 (8)	C(17)—H(15)	0.981 (14)

Table 4. Bond angles ( $^{\circ}$ ) with standard deviations in parentheses

C(1)—I—C(7)	98.65 (0.2)	C(9)—C(18)—N(1)	176.7 (0.9)
C(6)—C(1)—C(3)	123.5 (0.7)	C(10)—C(19)—N(2)	177.0 (0.8)
C(1)—C(2)—C(4)	119.4 (1.0)	C(1)—C(2)—H(1)	112.2 (9.5)
C(2)—C(3)—C(4)	119.0 (1.3)	C(3)—C(2)—H(1)	128.4 (9.6)
C(3)—C(4)—C(5)	121.4 (1.0)	C(2)—C(3)—H(2)	122.4 (7.9)
C(4)—C(5)—C(6)	120.3 (0.9)	C(4)—C(3)—H(2)	118.3 (8.0)
C(5)—C(6)—C(1)	116.4 (1.0)	C(3)—C(4)—H(3)	107.0 (8.0)
C(11)—C(8)—C(7)	110.3 (0.5)	C(5)—C(4)—H(3)	131.5 (7.9)
C(7)—C(8)—C(9)	107.1 (0.6)	C(4)—C(5)—H(4)	117.5 (2.0)
C(8)—C(9)—C(10)	107.0 (0.5)	C(6)—C(5)—H(4)	120.1 (1.7)
C(9)—C(10)—C(11)	108.7 (0.6)	C(1)—C(6)—H(5)	114.0 (3.5)
C(10)—C(11)—C(7)	107.0 (0.6)	C(5)—C(6)—H(5)	129.6 (3.5)
C(2)—C(1)—I	117.9 (0.5)	C(14)—C(13)—H(6)	108.9 (4.9)
C(6)—C(1)—I	118.6 (0.7)	O(2)—C(13)—H(6)	111.0 (4.7)
C(8)—C(7)—I	124.5 (0.5)	C(14)—C(13)—H(7)	109.0 (5.3)
C(11)—C(7)—I	125.2 (0.5)	O(2)—C(13)—H(7)	109.0 (6.8)
C(7)—C(8)—C(12)	127.4 (0.5)	H(6)—C(13)—H(7)	112.5 (7.3)
C(9)—C(8)—C(12)	125.4 (0.5)	C(13)—C(14)—H(8)	110.6 (5.4)
C(7)—C(11)—C(15)	126.8 (0.5)	C(13)—C(14)—H(9)	104.0 (8.4)
C(10)—C(11)—C(15)	126.3 (0.6)	C(13)—C(14)—H(10)	95.6 (8.1)
C(8)—C(9)—C(18)	129.1 (0.6)	H(8)—C(14)—H(9)	122.6 (9.9)
C(10)—C(9)—C(18)	123.9 (0.6)	H(8)—C(14)—H(10)	108.5 (10.3)
C(11)—C(10)—C(19)	129.4 (0.7)	H(9)—C(14)—H(10)	112.0 (11.3)
C(9)—C(10)—C(19)	121.8 (0.5)	C(17)—C(16)—H(11)	108.9 (11.4)
C(8)—C(12)—O(1)	125.2 (0.6)	O(4)—C(16)—H(11)	102.2 (10.5)
C(8)—C(12)—O(2)	111.6 (0.5)	C(17)—C(16)—H(12)	112.7 (8.3)
O(1)—C(12)—O(2)	123.1 (0.8)	O(4)—C(16)—H(12)	117.3 (11.1)
C(11)—C(15)—O(3)	123.5 (0.7)	H(11)—C(16)—H(12)	106.7 (14.0)
C(11)—C(15)—O(4)	111.4 (0.6)	C(16)—C(17)—H(13)	112.3 (1.1)
O(3)—C(15)—O(4)	125.1 (0.8)	C(16)—C(17)—H(14)	109.1 (1.6)
C(12)—O(2)—C(13)	117.4 (0.6)	C(16)—C(17)—H(15)	109.7 (1.5)
C(15)—O(4)—C(16)	115.6 (0.7)	H(13)—C(17)—H(14)	105.7 (1.5)
O(2)—C(13)—C(14)	106.2 (0.8)	H(13)—C(17)—H(15)	111.0 (1.7)
O(4)—C(16)—C(17)	108.4 (1.0)	H(14)—C(17)—H(15)	108.8 (1.2)

Fig. 2. Packing of the molecules viewed down  $c$ .

inside the van der Waals distance (3.5 Å). The free-electron pairs of the two O atoms delocalize the positive charge of the iodonium in connexion with the  $d$  orbitals of the I atom.

Due to this intramolecular charge compensation the intermolecular forces are merely van der Waals forces. This, along with the loose packing and the high temperature factors, is the reason for the twinning.

Table 5. Deviations (Å) of the atoms from the least-squares planes in the molecule

The atoms marked with an asterisk were not included in the computation of the planes.

$A = 7.13443$	C(1)	-0.007	C(5)	-0.001
$B = 8.08666$	C(2)	0.008	C(6)	0.003
$C = -1.83135$	C(3)	-0.005	I*	0.028
$D = 7.64941$	C(4)	0.001		
$A = 0.63525$	C(7)	0.002	C(12)*	-0.066
$B = 0.11278$	C(8)	-0.003	C(15)*	-0.024
$C = 14.19604$	C(9)	0.002	C(18)*	0.077
$D = 13.20101$	C(10)	-0.001	C(19)*	-0.023
	C(11)	-0.001	N(1)*	0.172
	I*	0.135	N(2)*	-0.027
$A = 1.02914$	I	0.019	C(12)	0.004
$B = -0.31353$	C(7)	-0.038	O(1)	-0.016
$C = 13.97601$	C(8)	0.031	O(2)*	-0.020
$D = 13.30311$				
$A = 0.08017$	I	0.027	C(15)	0.031
$B = -0.10304$	C(7)	-0.042	O(3)	-0.035
$C = 14.47586$	C(11)	0.020	O(4)*	0.082
$D = 12.99275$				

In the title compound, the charge compensation is intramolecular. The atoms I, O(1), C(12), C(8), C(7) and I, O(3), C(15), C(11), C(7) lie in two planes with an angle of  $175.79^{\circ}$  between them, and the distances I—O(1) (2.965 Å) and I—O(3) (3.138 Å) are well

Most of the calculations were performed with the XRAY 70 system of crystallographic programs (Stewart, Kundell & Baldwin, 1970). We wish to thank the 'Deutsche Forschungsgemeinschaft' for financial support, Dr K. Friedrich for a sample of the substance, and the 'Rechenzentrum Freiburg' for the facilities provided on the Univac 1106 computer.

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