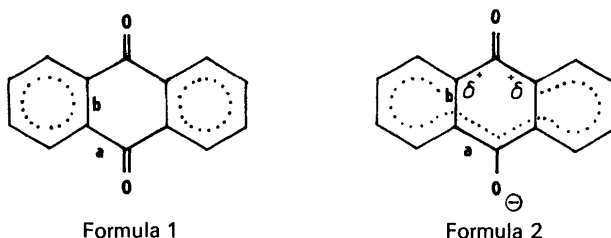


ring of the anthraquinone moiety, C(10)—C(11) [1.459 (9) Å] and C(10)—C(14) [1.461 (8) Å] are, in accordance with the above, shorter than C(5)—C(12) [1.516 (9) Å] and C(5)—C(13) [1.478 (8) Å], the latter showing almost pure C(sp<sup>2</sup>)—C(sp<sup>2</sup>) single-bond character. Bond lengths C(6)—C(13), C(4)—C(12), C(4)—C(3), C(3)—C(2), C(2)—C(1) and C(7)—C(8) correspond to an average value of the C—C bond length in benzene (1.39 Å). C(13)—C(14) and C(11)—C(12) bond lengths are about 0.03 Å shorter than those in structure (II).

The structure of the anthraquinone nucleus in the physcion molecule cannot be expressed by a single canonical formula showing the electronic configuration (corresponding to the normal quinoid structure of anthraquinone):



Formula 2 has been proposed as a second canonical form contributing to the electronic structure of the anthraquinone nucleus in the substituted anthracenedione derivatives (Ulický *et al.*, 1987). This represents an extension of  $\pi$ -electron delocalization from the benzene rings to the C(11)—C(10)—C(14) bridge resulting in a shifting of one half of the central ring from a quinoid to a benzenoid structure. While the difference in the relevant C—C bond length averages,  $\Delta = a - b$  [in our structure C(10)—C(11) =  $a$  and C(11)—C(12) =  $b$ ], is 0.07 (1) Å for

anthracenedione (formula 1) and  $\Delta = 0$  Å for formula 2, in the present structure  $\Delta = 0.056$  (12) Å. Thus, the structure of the anthraquinone nucleus is closer to formula 1.

The rings composed of atoms C(1), C(2), C(3), C(4), C(11), C(12) (*A*) and C(13), C(6), C(7), C(8), C(9), C(14) (*B*) do not show any significant deviations from planarity. In contrast, the central ring (*C*) displays slight but significant deviation from planarity. This is a consequence of twisting around the C(5)—C(12) and C(5)—C(13) bonds, with the dihedral angles O(18)—C(5)—C(12)—C(4) = 4.22 and O(18)—C(5)—C(13)—C(4) = -3.92°. As a result, the 14-membered ring system is also non-planar. The angles between the planes of the individual rings are: *AB* 2.2 (3), *C* 3.3 (3), *BC* 1.6 (2)°.

Thus it may be concluded that the crystal and molecular structure of the present compound is different from those of (I) and (II). Despite the presence of strong intramolecular hydrogen-bond interactions, no intermolecular interactions, such as those observed in (II), have been identified. This fact results in a greater contribution of the 'quinoid' formula to the resonance structure and in a lack of charge-transfer effect, the latter being evident in (II).

#### References

- JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
- PODOJIL, M., SEDMERA, P., VOKOUN, J., BETINA, V., BARÁTHOVÁ, H., ĎURÁČKOVÁ, Z., HORÁKOVÁ, K. & NEMEC, P. (1979). *Folia Microbiol. (Prague)*, **23**, 438–443.
- PRAKASH, A. (1967). *Acta Cryst.* **22**, 439–440.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- ULICKÝ, L., KETTMANN, V., SOLDÁNOVÁ, J. & BETINA, V. (1987). *Acta Cryst.* **C43**, 335–339.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1991). **C47**, 1881–1885

### 6,6-Dichloro-1-methyl-3,4,5-triphenylbicyclo[3.1.0]hex-3-en-2-one and 3-Chloro-2-methyl-4,5,6-triphenylphenol

BY JOHN C. BARNES,\* WILLIAM M. HORSPOOL AND FIONA I. MACKIE  
*Chemistry Department, The University, Dundee DD1 4HN, Scotland*

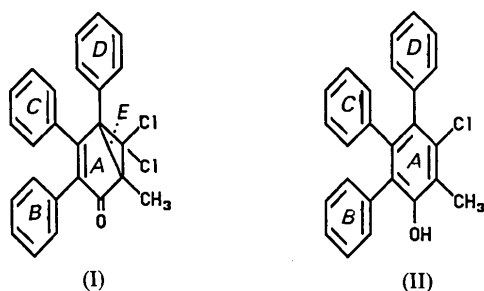
(Received 4 December 1990; accepted 7 February 1991)

**Abstract.** (I) C<sub>25</sub>H<sub>18</sub>Cl<sub>2</sub>O,  $M_r = 405.32$ , monoclinic,  $I2/a$ ,  $a = 23.95$  (2),  $b = 6.550$  (6),  $c = 26.59$  (2) Å,  $\beta = 96.4$  (1)°,  $V = 4145.2$  (10) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.298$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu =$

$2.95$  mm<sup>-1</sup>,  $F(000) = 1680$ ,  $T = 293$  K,  $R = 0.0735$  for 1700 reflexions. (II) C<sub>25</sub>H<sub>19</sub>ClO,  $M_r = 370.88$ , monoclinic,  $P2_1/n$ ,  $a = 12.211$  (8),  $b = 26.50$  (2),  $c = 12.477$  (9) Å,  $\beta = 99.12$  (1)°,  $V = 3986.4$  (8) Å<sup>3</sup>,  $Z =$

8,  $D_x = 1.236 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$ ,  $\mu = 0.20 \text{ mm}^{-1}$ ,  $F(000) = 1552$ ,  $T = 293 \text{ K}$ ,  $R = 0.091$  for 1625 reflexions. Photolysis of (I) gave the phenol (II) instead of the expected phenanthrene. There are no abnormal bond lengths or angles in either structure. The two unrelated molecules in (II) are connected by a weak hydrogen bond [3.15 (1)  $\text{\AA}$ ]. A loose cluster of four molecules is made up of centrosymmetrically related hydrogen-bonded pairs.

**Introduction.** Studies of the photochemical cyclizations to phenanthrenes of derivatives of tetraphenylcyclopentadienone and of 2,3-diphenylfuran (Horspool, 1971, 1984; Anderson & Horspool, 1971) have shown that *cis*-stilbene-type cyclizations (Mallory & Mallory, 1984) are chemically efficient under non-oxidative conditions providing the molecule under study has a leaving group to bring about the re-aromatization step.



In the present study, however, irradiation of 6,6-dichloro-3,4,5-triphenylbicyclo[3.1.0]hex-3-en-1-one (I) gave the phenol (II) with trace products which were not identified. Other tri-aryl analogues of (I) behaved similarly. The phenols are formed by the opening of the three-membered ring with loss of chlorine. This appears to arise from the singlet state since the reaction is not adversely affected by air or oxygen. Indeed the conversion of the parent bicyclohexenone was shown to occur in the solid when the irradiation of a thin film of (I) gave a 60% yield of (II).

The failure of (I) and its analogues to yield phenanthrenes on irradiation is difficult to explain. A comparison of (I) with cyclopentadienone derivatives which are known to undergo cyclization shows that there are few differences in the IR or UV spectra. The failure of the cyclization of the *cis*-stilbene moiety could be due to the inability of the aryl groups on C(2) and C(3) to adopt the correct alignment. This would mean that the aryl group on C(4) was in some way interfering. A comparison of molecular models of (I) and of tetraphenylcyclopentadienone did not suggest any significant differences. Cyclopropyl ketones readily undergo ring opening to aromatic species (Padwa, 1967) so that the failure

may be due to the ease with which the cyclopropyl ring opened. We have determined the crystal structures of (I) and (II) as a step towards clarifying the reaction sequence.

The crystallographic numbering scheme and the identification of the ring planes follows that adopted for tetraphenylcyclopentadiene (Barnes, Horspool & Mackie, 1991) for clarity in visualizing the relationships between the molecules.

**Experimental.** Photolyses were carried out in an immersion well apparatus with a Pyrex filter and a 400 W medium pressure Hg arc lamp. Solutions or suspensions of the adducts in anhydrous propan-2-ol were purged for 1 h with deoxygenated nitrogen and irradiated under a positive pressure of nitrogen. After irradiation the solvent was removed under reduced pressure and the products separated by chromatography on silica gel using mixtures of petroleum ether-toluene as eluant.

All calculations were performed on the University DEC 10 computer using *SHELX76* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978). Atomic scattering factors were taken from *SHELX76*.

**Compound (I).** Data were collected by equi-inclination Weissenberg photography on two crystals (0.75 × 0.31 × 0.14 mm) obtained from a chloroform-petroleum ether mixture.  $2\theta_{\text{max}} = 155^\circ$ . Layers  $h$  0:6  $l$  and  $hk$  0:18 gave 3217 observed reflexions reducing to 1704 unique reflexions with  $R_{\text{int}} = 0.0987$  covering the ranges  $-28 \leq h \leq 28$ ,  $0 \leq k \leq 6$ ,  $0 \leq l \leq 32$ . The unit cell was refined by a least-squares procedure using all measured reflexions during intensity measurement by the SERC Microdensitometer Service, Daresbury Laboratory. Data were corrected for the Lp terms but not for absorption.

The structure was solved by the direct methods routine *TANG* after adding 480 unobserved reflexions assigned  $F = 0.5F_{\text{min}}$ . These 480 data were used only for the direct methods stage. The structure was extended by least-squares refinement and difference syntheses to convergence using anisotropic thermal parameters for all non-H atoms. Methyl H atoms were located on a difference map and refined, phenyl group H atoms were placed on calculated positions with a single refined isotropic thermal parameter for each group. Final refinement (minimizing  $\sum w|F_o - |F_c||^2$ ), 274 refined parameters,  $R = 0.073$ ,  $wR = 0.095$ ,  $w = 1.000/[\sigma(F)^2 + 0.012939F^2]$ , mean shift/e.s.d. = 0.009, max. shift/e.s.d. = 0.090 (H atom), 0.012 (non-H atom), max. difference peak = 0.85, max. negative peak =  $-0.43 \text{ e \AA}^{-3}$ .

**Compound (II).** Crystals were grown from chloroform-petrol. Data were collected on a Stoe STADI II diffractometer. Data were collected using  $1.2^\circ \omega$  scans with stationary backgrounds. Cell

Table 1. Coordinates ( $\times 10^4$ ) and  $U_{eq}$  values ( $\times 10^3$ ) for non-H atoms of (I) with e.s.d.'s in parentheses

	$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$			
	x	y	z	$U_{eq}$ ( $\text{\AA}^2$ )
C(1)	9290 (2)	6488 (8)	9596 (2)	37 (1)
C(2)	9529 (2)	6314 (8)	9102 (2)	33 (1)
C(3)	9122 (2)	5696 (8)	8733 (2)	32 (1)
C(4)	8558 (2)	5349 (8)	8941 (2)	32 (1)
C(5)	8672 (2)	5814 (9)	9507 (2)	38 (1)
O(6)	9519 (2)	7103 (7)	9994 (2)	52 (1)
C(7)	10140 (2)	6582 (10)	9061 (2)	40 (1)
C(8)	10428 (3)	8354 (11)	9255 (2)	53 (2)
C(9)	10999 (3)	8547 (15)	9223 (3)	74 (3)
C(10)	11298 (3)	7002 (16)	9006 (3)	73 (3)
C(11)	11016 (3)	5254 (14)	8816 (3)	69 (3)
C(12)	10447 (3)	5044 (11)	8851 (2)	52 (2)
C(13)	9187 (2)	5402 (9)	8193 (2)	36 (1)
C(14)	9406 (2)	6995 (11)	7913 (2)	50 (2)
C(15)	9467 (3)	6769 (14)	7413 (3)	66 (2)
C(16)	9309 (3)	4888 (17)	7167 (3)	76 (3)
C(17)	9092 (3)	3323 (15)	7436 (3)	69 (2)
C(18)	9029 (2)	3559 (11)	7946 (2)	53 (2)
C(19)	8027 (2)	5894 (9)	8606 (2)	38 (1)
C(20)	7741 (2)	4398 (10)	8293 (2)	46 (2)
C(21)	7267 (3)	4915 (13)	7971 (3)	61 (2)
C(22)	7063 (3)	6944 (13)	7963 (3)	65 (2)
C(23)	7337 (3)	8400 (13)	8272 (3)	64 (2)
C(24)	7822 (3)	7909 (10)	8595 (3)	49 (2)
C(25)	8569 (2)	3610 (9)	9324 (2)	39 (1)
Cl(26)	7924 (1)	2511 (2)	9456 (1)	51 (1)
Cl(27)	9104 (1)	1721 (2)	9378 (1)	52 (1)
C(28)	8272 (3)	6864 (12)	9833 (3)	47 (2)

parameters were refined from 15 accurately centred reflexions. Layers  $h k 0:7$  were collected for a crystal  $0.54 \times 0.27 \times 0.16$  mm.  $2\theta_{max} = 50^\circ$ . No variation in intensity was observed for standard reflexions measured every 100 reflexions. The ranges collected were  $-13 < h < 13$ ,  $0 < k < 30$ ,  $0 < l < 7$  giving 5864 measured reflexions reducing to 5344 unique reflexions with  $R_{int} = 0.033$ . Only 1625 reflexions with  $|F| > 5\sigma(F)$  were used in the final refinement.

The direct methods routine *TANG* gave positions for 33 of the 54 unique non-H atoms of the two molecules forming the asymmetric unit. The structure was extended by conventional least-squares refinement and difference syntheses. Owing to the poor ratio of reliable reflexions per parameter all eight benzene rings were treated as rigid groups in the later stages of refinement. H atoms were placed on calculated positions except for the hydroxyl and methyl protons which were omitted. The H atoms of each phenyl group were assigned a single isotropic thermal parameter which was refined. All non-H atoms were given anisotropic thermal parameters in the final refinement. Final refinement (minimizing  $\sum w|F_o - |F_c||^2$ ), 422 refined parameters,  $R = 0.091$ ,  $wR = 0.114$ ,  $w = 3.3105/[\sigma(F)^2 + 0.002772F^2]$ , mean shift/e.s.d. = 0.074, max. shift/e.s.d. = 0.277, max. difference peak = 0.33, max. negative peak = -0.33 e  $\text{\AA}$ . The high final value of  $R$  reflects the weak diffraction pattern obtained from crystals of only moderate quality.

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for (I)

C(1)—O(6)	1.205 (7)	C(2)—C(1)	1.494 (8)
C(5)—C(1)	1.536 (8)	C(3)—C(2)	1.366 (7)
C(7)—C(2)	1.491 (8)	C(4)—C(3)	1.532 (8)
C(13)—C(3)	1.473 (8)	C(5)—C(4)	1.529 (8)
C(19)—C(4)	1.510 (7)	C(25)—C(4)	1.526 (8)
C(28)—C(5)	1.526 (10)	C(25)—C(5)	1.535 (8)
C(8)—C(7)	1.418 (9)	C(12)—C(7)	1.400 (9)
C(9)—C(8)	1.384 (10)	C(10)—C(9)	1.401 (13)
C(11)—C(10)	1.395 (13)	C(12)—C(11)	1.383 (10)
C(14)—C(13)	1.416 (9)	C(18)—C(13)	1.406 (9)
C(15)—C(14)	1.363 (10)	C(16)—C(15)	1.426 (13)
C(17)—C(16)	1.383 (13)	C(18)—C(17)	1.391 (10)
C(19)—C(20)	1.414 (8)	C(24)—C(19)	1.407 (9)
C(21)—C(20)	1.384 (9)	C(22)—C(21)	1.415 (12)
C(23)—C(22)	1.375 (11)	C(24)—C(23)	1.404 (9)
Cl(26)—C(25)	1.775 (6)	Cl(27)—C(25)	1.776 (6)
C(2)—C(1)—O(6)	127.9 (5)	C(5)—C(1)—O(6)	124.6 (5)
C(5)—C(1)—C(2)	107.4 (4)	C(3)—C(2)—C(1)	110.0 (5)
C(7)—C(2)—C(1)	122.1 (4)	C(7)—C(2)—C(3)	127.6 (5)
C(4)—C(3)—C(2)	111.8 (5)	C(13)—C(3)—C(2)	126.5 (5)
C(13)—C(3)—C(4)	121.7 (4)	C(5)—C(4)—C(3)	104.9 (4)
C(19)—C(4)—C(3)	118.0 (5)	C(19)—C(4)—C(5)	124.4 (5)
C(25)—C(4)—C(3)	113.6 (4)	C(25)—C(4)—C(5)	60.3 (4)
C(25)—C(4)—C(19)	121.4 (5)	C(4)—C(5)—C(1)	105.9 (5)
C(28)—C(5)—C(1)	116.0 (5)	C(28)—C(5)—C(4)	126.3 (5)
C(25)—C(5)—C(1)	116.0 (5)	C(25)—C(5)—C(4)	59.7 (4)
C(25)—C(5)—C(28)	121.0 (5)	C(8)—C(7)—C(2)	120.8 (5)
C(12)—C(7)—C(2)	120.5 (5)	C(12)—C(7)—C(8)	118.6 (5)
C(9)—C(8)—C(7)	119.7 (7)	C(10)—C(9)—C(8)	121.0 (8)
C(11)—C(10)—C(9)	119.4 (7)	C(12)—C(11)—C(10)	120.0 (7)
C(11)—C(12)—C(7)	121.3 (7)	C(14)—C(13)—C(3)	120.1 (5)
C(18)—C(13)—C(3)	121.0 (5)	C(18)—C(13)—C(14)	118.9 (5)
C(15)—C(14)—C(13)	121.3 (7)	C(16)—C(15)—C(14)	119.2 (7)
C(17)—C(16)—C(15)	120.0 (7)	C(18)—C(17)—C(16)	120.6 (8)
C(17)—C(18)—C(13)	119.9 (7)	C(20)—C(19)—C(4)	120.3 (5)
C(24)—C(19)—C(4)	120.2 (5)	C(24)—C(19)—C(20)	119.4 (5)
C(21)—C(20)—C(19)	120.3 (6)	C(22)—C(21)—C(20)	119.8 (7)
C(23)—C(22)—C(21)	120.1 (6)	C(24)—C(23)—C(22)	120.8 (7)
C(23)—C(24)—C(19)	119.5 (6)	C(5)—C(25)—C(4)	59.9 (4)
Cl(26)—C(25)—C(4)	118.9 (4)	Cl(26)—C(25)—C(5)	115.6 (4)
Cl(27)—C(25)—C(4)	122.2 (4)	Cl(27)—C(25)—C(5)	122.7 (4)
Cl(27)—C(25)—Cl(26)	109.8 (3)		

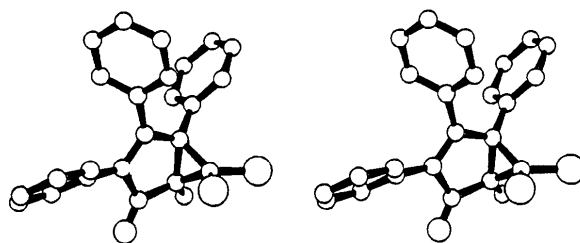


Fig. 1. Stereoview of molecule (I).

**Discussion.** Atomic coordinates and interatomic distances and angles for (I) are given in Tables 1\* and 2. The molecule is shown in Fig. 1. The cyclopropane ring *E* makes the cyclopentene ring *A* rigid and

\* 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 53992 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Coordinates ( $\times 10^4$ ) and  $U_{eq}$  values ( $\times 10^3$ ) for non-H atoms of (II) with e.s.d.'s in parentheses
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq} (\text{\AA}^2)$
C(1)	5091 (7)	695 (4)	6524 (6)	50 (6)
C(2)	4062 (7)	500 (4)	6064 (6)	38 (5)
C(3)	3404 (7)	759 (4)	5224 (6)	41 (5)
C(4)	3775 (7)	1213 (4)	4844 (6)	47 (5)
C(25)	4804 (7)	1408 (4)	5303 (6)	36 (5)
C(5)	5462 (7)	1149 (4)	6143 (6)	42 (5)
O(6)	5712 (7)	450 (3)	7360 (6)	42 (3)
C(7)	3664 (8)	26 (3)	6511 (8)	53 (6)
C(8)	4050 (8)	-452 (3)	6286 (8)	53 (6)
C(9)	3676 (8)	-877 (3)	6779 (8)	68 (7)
C(10)	2917 (8)	-825 (3)	7498 (8)	66 (7)
C(11)	2531 (8)	-347 (3)	7723 (8)	74 (7)
C(12)	2904 (8)	78 (3)	7230 (8)	38 (5)
C(13)	2323 (6)	532 (4)	4638 (7)	45 (5)
C(14)	2342 (6)	74 (4)	4088 (7)	44 (5)
C(15)	1356 (6)	-137 (4)	3562 (7)	69 (7)
C(16)	350 (6)	108 (4)	3586 (7)	103 (9)
C(17)	330 (6)	566 (4)	4136 (7)	72 (7)
C(18)	1317 (6)	778 (4)	4661 (7)	52 (6)
C(19)	3098 (7)	1511 (4)	3930 (9)	29 (5)
C(20)	3008 (7)	1349 (4)	2855 (9)	48 (6)
C(21)	2355 (7)	1618 (4)	2029 (9)	59 (6)
C(22)	1792 (7)	2050 (4)	2278 (9)	52 (6)
C(23)	1882 (7)	2212 (4)	3353 (9)	55 (6)
C(24)	2536 (7)	1943 (4)	4179 (9)	52 (6)
C(25)	4804 (7)	1408 (4)	5303 (6)	36 (5)
Cl(26)	5294 (3)	1956 (1)	4845 (3)	63 (1)
C(28)	6639 (10)	1344 (5)	6669 (12)	59 (5)
C(31)	8686 (7)	4276 (4)	5343 (7)	50 (6)
C(32)	8881 (7)	3813 (4)	4874 (7)	41 (5)
C(33)	8017 (7)	3563 (4)	4219 (7)	37 (5)
C(34)	6958 (7)	3775 (4)	4035 (7)	37 (5)
C(55)	6764 (7)	4238 (4)	4504 (7)	55 (6)
C(35)	7628 (7)	4488 (4)	5159 (7)	44 (5)
O(36)	9506 (7)	4547 (3)	6047 (7)	55 (3)
C(37)	16 (5)	3607 (3)	5111 (8)	29 (5)
C(38)	841 (5)	3808 (3)	4580 (8)	44 (5)
C(39)	1904 (5)	3600 (3)	4754 (8)	60 (7)
C(40)	2142 (5)	3192 (3)	5458 (8)	62 (7)
C(41)	1318 (5)	2991 (3)	5990 (8)	64 (6)
C(42)	255 (5)	3199 (3)	5816 (8)	58 (6)
C(43)	8278 (8)	3070 (3)	3739 (10)	45 (6)
C(44)	8836 (8)	3036 (3)	2848 (10)	55 (7)
C(45)	9090 (8)	2564 (3)	2457 (10)	74 (7)
C(46)	8787 (8)	2126 (3)	2957 (10)	61 (7)
C(47)	8228 (8)	2160 (3)	3848 (10)	72 (8)
C(48)	7974 (8)	2632 (3)	4239 (10)	58 (6)
C(49)	6051 (7)	3500 (3)	3303 (12)	36 (6)
C(50)	5996 (7)	3509 (3)	2176 (12)	71 (7)
C(51)	5135 (7)	3261 (3)	1513 (12)	92 (8)
C(52)	4328 (7)	3004 (3)	1975 (12)	68 (7)
C(53)	4383 (7)	2995 (3)	3102 (12)	76 (7)
C(54)	5244 (7)	3243 (3)	3765 (12)	64 (7)
Cl(56)	5452 (3)	4487 (1)	4251 (4)	85 (1)
C(58)	7325 (12)	4989 (5)	5778 (13)	78 (7)

Table 4. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for (II)

	Molecule X	Molecule Y	
C(1)—O(6)	1.354 (11)	1.417 (11)	
C(2)—C(7)	1.486 (13)	1.476 (11)	
C(3)—C(13)	1.527 (11)	1.491 (14)	
C(4)—C(19)	1.519 (13)	1.507 (13)	
C(5)—C(28)	1.570 (15)	1.607 (18)	
C(25)—Cl(26)	1.703 (10)	1.715 (9)	
O(6)—C(1)—C(2)	119.7 (8)	123.7 (7)	
O(6)—C(1)—C(5)	120.2 (8)	116.3 (8)	
C(7)—C(2)—C(1)	119.1 (7)	117.2 (7)	
C(7)—C(2)—C(3)	120.9 (8)	122.8 (8)	
C(13)—C(3)—C(2)	121.2 (8)	117.4 (8)	
C(13)—C(3)—C(4)	118.6 (7)	118.6 (7)	
C(19)—C(4)—C(3)	122.4 (7)	118.5 (8)	
C(19)—C(4)—C(25)	117.6 (8)	121.4 (7)	
Cl(26)—C(25)—C(4)	121.3 (7)	118.5 (6)	
Cl(26)—C(25)—C(5)	118.7 (7)	121.5 (7)	
C(28)—C(5)—C(1)	117.9 (8)	122.1 (8)	
C(28)—C(5)—C(25)	122.1 (9)	117.6 (8)	
Short intermolecular contacts			
O(6)...O(36)	3.148 (12)	O(36)...O(36')	3.879 (12)

ring *A*, compared with 35.3 (4), 47.3 (5) $^\circ$  in tetraphenylcyclopentadienone. The three phenyl groups are arranged like blades of a propeller about ring *A* in spite of the displacement of ring *D* caused by C(4) having distorted tetrahedral bonding geometry. The normal to ring *D* lies at 78.5 (5) $^\circ$  to the normal to plane *A*. The torsion angle C(28)—C(5)—C(4)—C(19) is 1.2 (4) $^\circ$ .

Atomic coordinates and interatomic distances and angles for (II) are given in Tables 3 and 4. The relatively low precision of this determination makes an extended discussion inappropriate but the structure shows several interesting features. The only significant differences between the two crystallographically unique molecules *X* and *Y* are found in the torsion angles about ring *A* [e.g. Cl(26)—C(25)—C(5)—C(28)] with several differences in the range 7–8 $^\circ$  and in the angles between the normals to mean planes of rings *A* and *C* which are discussed below. The presence of three adjacent phenyl groups and three other substituents on the benzene ring *A* leads to considerable crowding. Intramolecular angles between normals to the peripheral phenyl groups and rings *AX* or *AY* lie between 75.0 and 78.1 $^\circ$ , except for *CX/AX* which is reduced to 63.6 (5) $^\circ$  to minimize contact with *DY'*, see below. The average value of 74.4 $^\circ$  can be compared with 52.3 $^\circ$  in *o*-diphenylbenzene with only two substituents (Aikawa, Maruyama, Ohashi & Sasada, 1978) and 42.9 $^\circ$  in tetraphenylcyclopentadienone (Barnes, Horspool & Mackie, 1991) where the five-membered ring allows more space between the phenyl groups.

Fig. 2 shows that the unique molecules are connected by a weak hydrogen bond [3.15 (1)  $\text{\AA}$ ] linking the OH groups O(6) and O(36). There are no other

almost planar; the r.m.s. deviation of atoms C(1)—C(5) from their mean plane is 0.011  $\text{\AA}$ . The angle between the normals to planes *A* and *E* is 109.7 (5) $^\circ$ . Plane *F* [C(25), Cl(26), Cl(27)] has its normal at 87.9 (5) $^\circ$  to that of plane *E* and 90.0 (5) $^\circ$  to that of plane *A*. Cl(27) lies 2.76  $\text{\AA}$  above the centre of plane *A*, compared with a sum of van der Waals radii of 3.4  $\text{\AA}$ , suggesting some interaction between Cl(27) and ring *A*. The normals to phenyl groups *B* and *C* make angles of 52.3 (5), 53.2 (6) $^\circ$  to the normal to

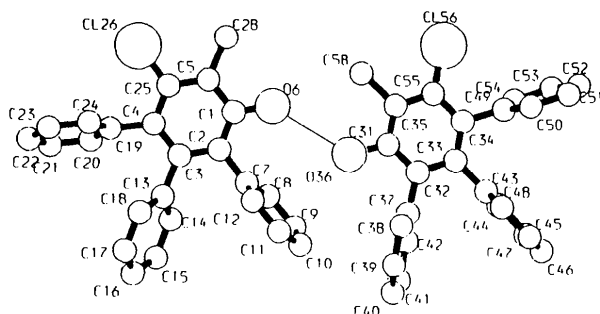


Fig. 2. View of (II) perpendicular to plane C(1)–C(5), showing hydrogen bond between crystallographically independent molecules.

close contacts between the  $XY$  pair. The angle between the normals to planes  $AX$  and  $AY$  is  $13.4(5)^\circ$ . These rings are approximately coplanar; the average deviation of an atom of  $AY$  from the mean plane of  $AX$  is  $0.081 \text{ \AA}$ . This bimolecular fragment is close to a centre of inversion, giving a four-molecule cluster in the  $c$  direction (Fig. 3) in which  $O(36)\cdots O(36')$  is  $3.88(1) \text{ \AA}$ . There are no other short contacts between  $XY$  and  $XY'$ ; molecule  $X$  partially overlays  $Y'$  in the  $c$  direction with the average separation of the planes  $AX$  and  $AY$   $4.8 \text{ \AA}$ . There is no  $\pi$  overlap between these molecules. The rings closest to  $AX$  and  $AY$  are  $CY'$  and  $BX'$  respectively, with intermolecular angles between normals to planes  $91.3(5)$  and  $64.7(5)^\circ$ .

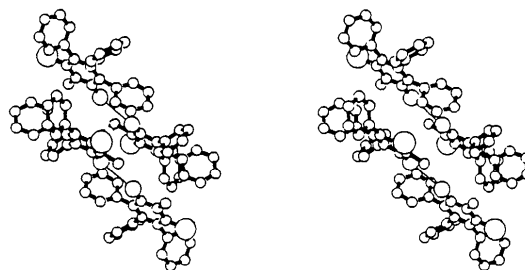


Fig. 3. Stereoview of (II) along the orthogonal axis  $XO$  showing the relationship between pairs of independent molecules related across the centre of inversion.

#### References

- AIKAWA, S., MARUYAMA, Y., OHASHI, Y. & SASADA, Y. (1978). *Acta Cryst.* **B34**, 2901–2904.  
 ANDERSON, D. T. & HORSPPOOL, W. M. (1971). *J. Chem. Soc. Chem. Commun.* p. 615.  
 BARNES, J. C., HORSPPOOL, W. M. & MACKIE, F. I. (1991). *Acta Cryst.* **C47**, 164–168.  
 HORSPPOOL, W. M. (1971). *J. Chem. Soc. C*, pp. 400–404.  
 HORSPPOOL, W. M. (1984). *J. Photochem.* **24**, 122–123.  
 MALLORY, F. B. & MALLORY, C. W. (1984). *Org. Reactions*, **30**, 1–456.  
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.  
 PADWA, A. (1967). *Org. Photochem.* **1**, 91–126.  
 ROBERTS, P. & SHELDRIK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1991). **C47**, 1885–1888

## Structure of 4-[(1-Amidinihydroazono)ethyl]-5-methyl-1-pyrazolecarboxamidium Dichloride Monohydrate

BY ALAIN COUSSON

*Institut Curie, Section de Physique et Chimie, UA CNRS 448, 11 rue Pierre et Marie Curie, 75231 Paris CEDEX 05, France*

BERNARD BACHET

*Laboratoire de Minéralogie et Cristallographie, LA CNRS 09, Université Pierre et Marie Curie, 4 Place Jussieu, 75230 Paris CEDEX 05, France*

AND BRUNO KOKEL AND MICHEL HUBERT-HABART

*Institut Curie, Section de Physique et Chimie, Chercheurs INSERM, 11 rue Pierre et Marie Curie, 75231 Paris CEDEX 05, France*

(Received 15 November 1990; accepted 25 January 1991)

**Abstract.**  $[C_8H_{16}N_8]^{2+} \cdot 2Cl^- \cdot H_2O$ ,  $M_r = 313.19$ , triclinic,  $P\bar{1}$ ,  $a = 9.069(3)$ ,  $b = 10.781(4)$ ,  $c = 7.810(4) \text{ \AA}$ ,  $\alpha = 108.68(3)$ ,  $\beta = 100.68(3)$ ,  $\gamma =$

$86.68(4)^\circ$ ,  $V = 711(6) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 1.463 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Cu K}\alpha) = 1.5418 \text{ \AA}$ ,  $\mu = 0.43 \text{ mm}^{-1}$ ,  $F(000) = 328$ ,  $T = 293 \text{ K}$ . The structure