

Structures of *cis*-1,2-Bis(4-cyanophenyl)-1,2-bis(4-methoxyphenyl)cyclopropane (I), 1,1-Bis(4-cyanophenyl)-2,2-diphenylcyclopropane (II) and *trans*-1-(4-Cyanophenyl)-2-(4-methoxyphenyl)-1,2-diphenylcyclopropane (III)*

BY T. STANLEY CAMERON, ANTHONY LINDEN AND K. JOCHEM

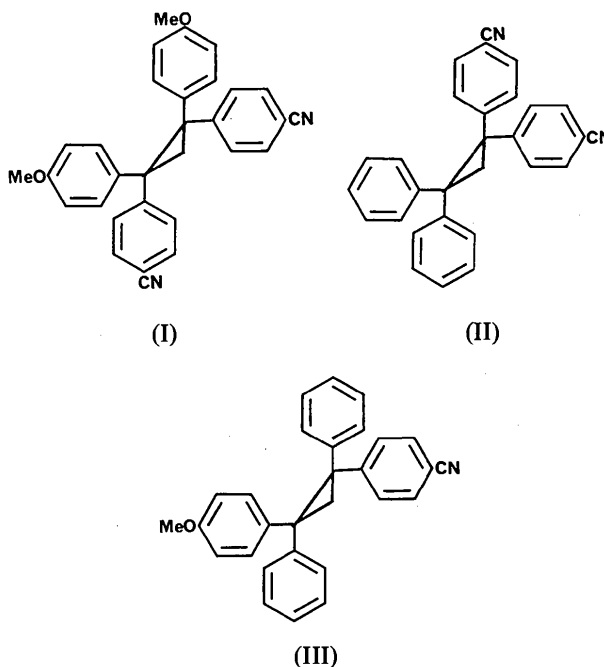
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada

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Abstract. (I), $C_{31}H_{24}N_2O_2$, $M_r = 456.5$, monoclinic, $C2/c$, $a = 18.59$ (2), $b = 8.615$ (3), $c = 31.61$ (3) Å, $\beta = 98.85$ (5)°, $V = 5002$ (12) Å³, $Z = 8$, $D_x = 1.212$ g cm⁻³, Mo $K\alpha$ radiation (graphite monochromated), $\lambda = 0.70926$ Å, $\mu = 0.71$ cm⁻¹, $F(000) = 1920$, $T = 293$ K, 1266 observed reflections with $I > \sigma(I)$, final $R = 0.040$. (II), $C_{29}H_{20}N_2$, $M_r = 396.5$, monoclinic, $P2_1/c$, $a = 9.962$ (6), $b = 11.801$ (3), $c = 18.311$ (3) Å, $\beta = 101.63$ (3)°, $V = 2108$ (2) Å³, $Z = 4$, $D_x = 1.249$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70926$ Å, $\mu = 0.68$ cm⁻¹, $F(000) = 832$, $T = 293$ K, 1207 observed reflections with $I > \sigma(I)$, final $R = 0.045$. (III), $C_{29}H_{23}NO$, $M_r = 399.5$, hexagonal, $P6_1$, $a = 21.402$ (5), $c = 9.018$ (7) Å, $V = 3577$ (4) Å³, $Z = 6$, $D_x = 1.113$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.70926$ Å, $\mu = 0.62$ cm⁻¹, $F(000) = 1260$, $T = 293$ K, 657 observed reflections with $I > \sigma(I)$, final $R = 0.076$. π -Electron conjugation is indicated by a long cyclopropane ring bond between the C atoms to which the substituents are bonded [1.57 Å in (I) and (II), 1.54 Å in (III)]. For each compound, one substituent on each cyclopropane C atom adopts the 'perpendicular' orientation, while the other substituent does not adopt any special orientation. This suggests that π -electron donation from the phenyl groups to the cyclopropane ring may be occurring.

Introduction. The molecular structures of many substituted cyclopropanes have been reported and are summarized by Lauher & Ibers (1975),† Jason & Ibers (1977) and Allen (1980, 1981). Examination of all of these structures shows that substitution may cause major changes in the geometry of the cyclopropane ring. In particular, those substituents with π

orbitals can conjugate with the cyclopropane ring. However, the effects of π -orbital-containing ligands on the geometry of the cyclopropane ring have been shown to vary considerably with the type, number and location of substituents (Lauher & Ibers, 1975; Jason & Ibers, 1977; Allen, 1980, 1981). Jason & Ibers have discussed the orbital and resultant orientational requirements for conjugation between substituents and the cyclopropane ring, and have shown that for π -electron donation from the cyclopropane ring to the substituent, the substituent must adopt the 'bisecting' orientation, while both the 'bisecting' and 'perpendicular' orientations are allowed if the substituent is the π -electron donor. This report presents a structural investigation of three *para*-substituted 1,1,2,2-tetraphenyl cyclopropanes. The cyclopropane bond lengths and the orientation of the π systems of the substituents are compared with other substituted cyclopropanes.



* 4,4'-[1,2-(4-Methoxyphenyl)cycloprop-1,2-ylene]dibenzonitrile, 4,4'-(2,2-diphenylcycloprop-1-ylidene)dibenzonitrile and 4-[2-(4-methoxyphenyl)-1,2-diphenylcycloprop-1-yl]benzonitrile, respectively.

† Lauher & Ibers (1975) contains several errors in the references. For the correct citations for references 8 and 12 therein see Long, Maddox & Trueblood (1969) and Declercq, Piret & Van Meerseche (1972). Reference 12 in the text (p. 564) is listed as reference 14.

Experimental. (I)–(III) were prepared and recrystallized as described previously (Arnold, Wayner & Yoshida, 1982). Enraf–Nonius CAD-4 diffractometer, lattice parameters from 25 reflections with $\theta = 10\text{--}12^\circ$, $\omega\text{--}2\theta$ scans, ω -scan width = $(1.0 + 0.35 \tan \theta)^\circ$ at $0.6\text{--}3.3^\circ \text{ min}^{-1}$, extended 25% on each side for background measurement, three standard reflections (no decay), intensities reduced to a standard scale (Cameron & Cordes, 1979), L_p corrections applied, no corrections for absorption. The structures were solved by direct-methods routines (Germain, Main & Woolfson, 1971; Sheldrick, 1976) from which all of the non-H atoms were located. All H atoms were placed in their geometrically calculated positions [$d(\text{C—H}) = 1.08 \text{ \AA}$] and allowed to ride on the atoms to which they were bonded. Anisotropic refinement (on F) of the non-H atoms and refinement of individual isotropic temperature factors on the H atoms employed a five-block-matrix least-squares method (Sheldrick, 1976), which minimized $\sum w(|F_o| - |F_c|)^2$ where w is the weight. Scattering factors for neutral atoms were those recorded in *International Tables for X-ray Crystallography* (1974) and were corrected for anomalous dispersion.

(I): Crystal $0.2 \times 0.25 \times 0.35 \text{ mm}$, intensities for $\theta < 23^\circ$, hkl : -20 to 20 , 0 to 9 , 0 to 34 , 3815 reflections measured, 3441 unique ($R_{\text{int}} = 0.043$). Refinement converged at $R = 0.040$, $wR = 0.042$ for 1266 observed reflections with $I > \sigma(I)$, weight = $[\sigma^2(F_o) + 0.0112|F_o|^2]^{-1}$, 351 parameters, $S = 3.04$, $(\Delta/\sigma)_{\text{max}} = 0.7$, max. and min. heights in the final difference Fourier map = 0.12 and -0.13 e \AA^{-3} , seven reflections were omitted because of suspected extinction.

(II): Crystal $0.25 \times 0.25 \times 0.3 \text{ mm}$, intensities for $\theta < 20^\circ$, hkl : 0 to 9 , 0 to 11 , -17 to 17 , 2182 reflections measured, 1899 unique ($R_{\text{int}} = 0.049$). Refinement converged at $R = 0.045$, $wR = 0.047$ for 1207 observed reflections with $I > \sigma(I)$, weight = $0.077/[\sigma^2(F_o) + 0.0047|F_o|^2]$, 310 parameters, $S = 1.50$, $(\Delta/\sigma)_{\text{max}} = 0.4$, max. and min. heights in the final difference Fourier map = 0.17 and -0.20 e \AA^{-3} , one reflection was omitted because of suspected extinction.

(III): Several attempts were made to collect data for this compound using different crystals. The crystals were generally of poor quality. In each case many of the possible reflections were unobserved and no significant intensities could be recorded at $\theta > 20^\circ$. The results reported here are derived from the best data set obtainable and are included for completeness. Anything other than the gross features of this structure should be treated with caution. Crystal $0.2 \times 0.15 \times 0.4 \text{ mm}$, intensities for $\theta < 20^\circ$, hkl : -20 to 20 , 0 to 20 , 0 to 8 , 3675 reflections measured, 1204 unique ($R_{\text{int}} = 0.123$). Because of the paucity of data, only the methoxy and cyano groups were

refined anisotropically, the remaining non-H atoms being refined isotropically. The origin was defined by fixing the z coordinate of the O atom. Refinement converged at $R = 0.076$, $wR = 0.071$ for 657 observed reflections with $I > \sigma(I)$, weight = $0.069/[\sigma^2(F_o) + 0.008|F_o|^2]$, 171 parameters, $S = 3.17$, $(\Delta/\sigma)_{\text{max}} = 0.4$, max. and min. heights in the final difference Fourier map = 0.23 and -0.26 e \AA^{-3} , one reflection was omitted because of suspected extinction.

Discussion. Atomic positional parameters for (I)–(III) are listed in Tables 1–3 respectively. Selected bond lengths and angles for each complex are given in Table 4.* The molecular structures of the three cyclopropane derivatives are very similar in spite of the different space groups and variation of the phenyl substituents. Views of the molecules with their numbering schemes are shown in Figs. 1–3.

The geometries of the phenyl rings are normal, the average C—C bond length being 1.388 (10), 1.384 (11) and 1.38 (1) \AA for (I), (II) and (III) respectively. The phenyl rings are planar with no atom deviating by more than 0.025 \AA from the best least-squares plane. The C—C bonds between the cyclopropane ring and the α carbon of each phenyl ring average 1.513 (13), 1.500 (15) and 1.50 (1) \AA for (I), (II) and (III) respectively, which is consistent with the corresponding bond length observed in other phenyl-substituted cyclopropanes (Jason & Ibers, 1977; Allen, 1980, 1981). In agreement with the findings of Jason & Ibers, the presence of substituents on the phenyl groups has no significant effect on these bond lengths. The bond angles formed by the phenyl substituents at C1 and C2, which range from 110.8 to 117.2° (Table 4), also compare well with those found previously for cyclopropanes with *gem*-phenyl substituents [113.9 and 113.5° (Lauher & Ibers, 1975); 113.0° (Ahmed & Gabe, 1964); 115.3° (DeLacy & Kennard, 1972)]. The variation in these angles is probably the result of steric interactions between adjacent phenyl groups with different substituents in the 4 position, rather than being related in any way to the strength of bonding interactions with the cyclopropane rings.

The cyclopropane ring in each of the structures has unequal C—C bond lengths with the C1—C2 bond between the phenyl substituents being the longest in each case. While the C2—C3 and C1—C3 bond lengths in each compound are not significantly different from the C—C bond lengths in cyclo-

* Lists of anisotropic thermal parameters, H-atom positions, interatomic distances, bond angles, torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52948 (58 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional positional and equivalent isotropic thermal parameters (Å²) for (I) with e.s.d.'s in parentheses

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C1	0.6315 (2)	-0.1515 (5)	0.6108 (1)	0.0629
C2	0.6881 (2)	-0.2661 (5)	0.6367 (1)	0.0632
C3	0.7103 (2)	-0.1059 (6)	0.6250 (1)	0.0717
C11	0.6057 (2)	-0.1884 (5)	0.5649 (1)	0.0696
C12	0.5341 (2)	-0.2351 (7)	0.5505 (1)	0.0847
C13	0.5107 (3)	-0.2846 (8)	0.5092 (1)	0.0896
C14	0.5595 (3)	-0.2877 (7)	0.4800 (1)	0.0760
C15	0.6294 (3)	-0.2366 (7)	0.4922 (1)	0.0873
C16	0.6521 (3)	-0.1863 (7)	0.5335 (1)	0.0870
C17	0.5355 (3)	-0.3522 (8)	0.4377 (2)	0.0960
N1	0.5175 (2)	-0.4120 (7)	0.4052 (1)	0.1088
C21	0.5771 (2)	-0.0773 (6)	0.6359 (1)	0.0607
C22	0.5237 (2)	-0.1615 (5)	0.6511 (1)	0.0598
C23	0.4740 (2)	-0.0934 (5)	0.6747 (1)	0.0600
C24	0.4787 (2)	0.0634 (6)	0.6830 (1)	0.0703
C25	0.5311 (3)	0.1509 (6)	0.6674 (1)	0.0795
C26	0.5801 (2)	0.0810 (6)	0.6440 (1)	0.0742
O1	0.4342 (2)	0.1439 (4)	0.7066 (1)	0.0921
C27	0.3832 (3)	0.0539 (7)	0.7261 (2)	0.0949
C31	0.6811 (2)	-0.3023 (5)	0.6832 (1)	0.0567
C32	0.6363 (2)	-0.4211 (5)	0.6936 (1)	0.0625
C33	0.6290 (2)	-0.4512 (5)	0.7364 (1)	0.0634
C34	0.6675 (2)	-0.3654 (5)	0.7688 (1)	0.0639
C35	0.7156 (2)	-0.2509 (6)	0.7593 (1)	0.0699
C36	0.7209 (2)	-0.2197 (5)	0.7166 (1)	0.0647
O2	0.6631 (1)	-0.3832 (4)	0.8116 (1)	0.0797
C37	0.6096 (3)	-0.4870 (6)	0.8236 (1)	0.0878
C41	0.7158 (2)	-0.4010 (6)	0.6132 (1)	0.0651
C42	0.6708 (2)	-0.5186 (6)	0.5953 (1)	0.0714
C43	0.6979 (3)	-0.6456 (6)	0.5762 (1)	0.0765
C44	0.7719 (3)	-0.6556 (7)	0.5746 (1)	0.0727
C45	0.8187 (3)	-0.5411 (7)	0.5934 (1)	0.0749
C46	0.7907 (2)	-0.4146 (7)	0.6124 (1)	0.0704
C47	0.8008 (3)	-0.7897 (9)	0.5551 (2)	0.0986
N2	0.8236 (3)	-0.8942 (8)	0.5395 (2)	0.1427

Table 2. Fractional positional and equivalent isotropic thermal parameters (Å²) for (II) with e.s.d.'s in parentheses

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C1	0.2468 (4)	0.4173 (3)	0.2563 (2)	0.0427
C2	0.3512 (4)	0.3158 (4)	0.2643 (2)	0.0454
C3	0.3913 (4)	0.4263 (3)	0.3026 (2)	0.0466
C11	0.2129 (4)	0.4834 (3)	0.1858 (2)	0.0434
C12	0.0761 (5)	0.5052 (4)	0.1528 (2)	0.0511
C13	0.0390 (5)	0.5685 (4)	0.0885 (2)	0.0520
C14	0.1391 (5)	0.6126 (4)	0.0545 (2)	0.0493
C15	0.2766 (5)	0.5933 (4)	0.0861 (2)	0.0561
C16	0.3118 (5)	0.5301 (4)	0.1503 (2)	0.0520
C17	0.1022 (5)	0.6800 (4)	-0.0115 (3)	0.0539
N1	0.0736 (5)	0.7324 (4)	-0.0659 (3)	0.0789
C21	0.1329 (4)	0.4089 (4)	0.2988 (2)	0.0421
C22	0.1196 (5)	0.4892 (4)	0.3516 (2)	0.0565
C23	0.0082 (5)	0.4871 (4)	0.3869 (3)	0.0610
C24	-0.0887 (4)	0.4028 (4)	0.3694 (2)	0.0500
C25	-0.0755 (4)	0.3199 (4)	0.3177 (2)	0.0464
C26	0.0352 (4)	0.3232 (4)	0.2826 (2)	0.0433
C27	-0.2093 (6)	0.4021 (4)	0.4045 (3)	0.0619
N2	-0.3015 (5)	0.4012 (4)	0.4322 (2)	0.0561
C31	0.3315 (4)	0.2135 (3)	0.3117 (2)	0.0418
C32	0.3762 (5)	0.2142 (4)	0.3885 (2)	0.0528
C33	0.3676 (5)	0.1171 (4)	0.4298 (2)	0.0568
C34	0.3151 (4)	0.0176 (4)	0.3957 (2)	0.0527
C35	0.2682 (5)	0.0187 (4)	0.3195 (3)	0.0537
C36	0.2763 (4)	0.1138 (4)	0.2785 (2)	0.0466
C41	0.4092 (4)	0.2811 (3)	0.1992 (2)	0.0451
C42	0.3273 (5)	0.2440 (4)	0.1324 (2)	0.0572
C43	0.3862 (6)	0.1985 (4)	0.0777 (3)	0.0682
C44	0.5292 (7)	0.1915 (4)	0.0870 (3)	0.0768
C45	0.6084 (6)	0.2307 (4)	0.1517 (3)	0.0715
C46	0.5517 (5)	0.2736 (4)	0.2075 (3)	0.0552

Table 3. Fractional positional and equivalent isotropic thermal parameters (Å²) for (III) with e.s.d.'s in parentheses

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{iso} or U_{eq}
C1	0.1497 (6)	0.7844 (6)	0.3481 (16)	0.046 (4)
C2	0.1101 (6)	0.7031 (5)	0.3119 (16)	0.035 (3)
C3	0.0877 (6)	0.7516 (6)	0.2391 (17)	0.049 (4)
C11	0.1379 (6)	0.8085 (6)	0.4946 (17)	0.037 (3)
C12	0.0727 (9)	0.7957 (8)	0.5455 (20)	0.068 (5)
C13	0.0607 (9)	0.8172 (8)	0.6837 (21)	0.067 (5)
C14	0.1187 (9)	0.8498 (8)	0.7817 (21)	0.068 (5)
C15	0.1850 (9)	0.8640 (8)	0.7330 (21)	0.067 (5)
C16	0.1942 (8)	0.8408 (7)	0.5936 (19)	0.061 (4)
O	0.1122 (6)	0.8728 (6)	0.9195	0.0726
C17	0.0475 (9)	0.8628 (10)	0.9720 (20)	0.0950
C21	0.2240 (6)	0.8296 (6)	0.2822 (16)	0.045 (4)
C22	0.2788 (6)	0.8182 (7)	0.3213 (17)	0.052 (4)
C23	0.3472 (8)	0.8595 (8)	0.2583 (19)	0.063 (4)
C24	0.3598 (9)	0.9139 (8)	0.1639 (21)	0.069 (4)
C25	0.3075 (8)	0.9287 (9)	0.1292 (21)	0.081 (5)
C26	0.2369 (7)	0.8868 (7)	0.1881 (17)	0.060 (4)
C31	0.1484 (6)	0.6741 (7)	0.2216 (17)	0.043 (4)
C32	0.1765 (6)	0.6362 (6)	0.2907 (17)	0.043 (4)
C33	0.2140 (7)	0.6096 (7)	0.2152 (18)	0.054 (4)
C34	0.2279 (8)	0.6238 (8)	0.0674 (20)	0.063 (4)
C35	0.2001 (7)	0.6588 (7)	-0.0129 (20)	0.061 (4)
C36	0.1599 (8)	0.6849 (8)	0.0699 (20)	0.069 (5)
C37	0.2677 (9)	0.5939 (9)	-0.0092 (19)	0.0661
N	0.3023 (8)	0.5765 (9)	-0.0583 (17)	0.0812
C41	0.0597 (6)	0.6507 (6)	0.4235 (15)	0.038 (3)
C42	-0.0085 (6)	0.6007 (6)	0.3795 (18)	0.048 (4)
C43	-0.0538 (8)	0.5469 (7)	0.4788 (19)	0.063 (4)
C44	-0.0290 (8)	0.5410 (8)	0.6127 (19)	0.071 (4)
C45	0.0374 (7)	0.5893 (7)	0.6616 (19)	0.056 (4)
C46	0.0836 (7)	0.6445 (6)	0.5633 (17)	0.048 (4)

propane (1.510 Å; Bastiansen, Fritsch & Hedberg, 1964), the C1—C2 bond [1.575 (7) Å in (I) and 1.573 (6) Å in (II)] are among the longest observed in any substituted cyclopropane. Similar long C—C bonds in cyclopropanes (greater than 1.5 Å) are found in 1,1,2,2-tetracyanocyclopropane [1.560 (2) Å] (Lemley, Skarstad & Hughes, 1976; Wang & Stucky, 1973), 1,1-difluorocyclopropane [1.553 (1) Å] (Perretta & Laurie, 1975), 1-chlorophenyl-1-cyano-2-dimethylaminophenylcyclopropane [1.580 Å] (Meunier-Piret & Van Meerssche, 1971) and 2,5-dimethyl-7,7-dicyanonorcaradiene [1.559 Å] (Fritchie, 1966). The C1—C2 bond of (III) appears to be longer than the C2—C3 and C1—C3 bonds; however, the high e.s.d.'s on the atomic positional parameters of this structure prevent any definitive comparisons being made.

It has been shown (Lauher & Ibers, 1975) that those cyclopropanes with substituents which are not capable of π interactions have ring structures in which all three C—C bond lengths are similar, while lengthening and shortening of bonds in the cyclopropane ring suggests that some form of conjugation is occurring. However, changes in cyclopropane C—C bond lengths do not aid the determination of whether the substituent is interacting *via* donation or withdrawal of π electrons from the cyclopropane

ring. As shown by Hoffman (1970), transfer of π -electron density from the cyclopropane ring to a substituent will weaken adjacent bonds, since the

Table 4. Selected bond lengths (Å) and angles (°) for (I), (II) and (III) with *e.s.d.*'s in parentheses

(I)			
C1—C2	1.575 (7)	C14—C17	1.453 (9)
C1—C3	1.517 (7)	C17—N1	1.152 (9)
C2—C3	1.503 (7)	C24—O1	1.382 (7)
C1—C11	1.493 (7)	O1—C27	1.435 (7)
C1—C21	1.517 (7)	C34—O2	1.377 (6)
C2—C31	1.511 (7)	O2—C37	1.431 (7)
C2—C41	1.529 (7)	C44—C47	1.452 (9)
C11—C16	1.411 (8)	C47—N2	1.139 (10)
C13—C14	1.393 (8)		
C2—C1—C3	58.1 (3)	C1—C2—C41	118.5 (4)
C1—C2—C3	59.0 (3)	C3—C2—C31	117.3 (4)
C1—C3—C2	62.9 (3)	C3—C2—C41	119.4 (4)
C2—C1—C11	117.4 (4)	C31—C2—C41	113.7 (4)
C2—C1—C21	116.1 (4)	C14—C17—N1	175.9 (7)
C3—C1—C11	119.6 (4)	C24—O1—C27	116.7 (4)
C3—C1—C21	115.3 (4)	C34—O2—C37	118.6 (4)
C11—C1—C21	117.2 (4)	C44—C47—N2	179.4 (7)
C1—C2—C31	118.6 (4)		
(II)			
C1—C2	1.573 (6)	C2—C41	1.484 (7)
C1—C3	1.520 (7)	C14—C17	1.432 (7)
C2—C3	1.496 (7)	C17—N1	1.157 (8)
C1—C11	1.490 (6)	C24—C27	1.472 (8)
C1—C21	1.503 (6)	C27—N2	1.136 (8)
C2—C31	1.522 (7)		
C2—C1—C3	57.8 (3)	C1—C2—C31	119.9 (4)
C1—C2—C3	59.3 (3)	C1—C2—C41	119.5 (4)
C1—C3—C2	62.9 (3)	C3—C2—C31	118.4 (4)
C2—C1—C11	120.6 (4)	C3—C2—C41	120.5 (4)
C2—C1—C21	117.1 (4)	C31—C2—C41	110.8 (4)
C3—C1—C11	118.1 (4)	C14—C17—N1	178.3 (6)
C3—C1—C21	116.4 (4)	C24—C27—N2	179.4 (6)
C11—C1—C21	114.9 (4)		
(III)			
C1—C2	1.54 (2)	C2—C41	1.49 (2)
C1—C3	1.51 (2)	C14—O	1.37 (2)
C2—C3	1.49 (2)	O—C17	1.37 (2)
C1—C11	1.49 (2)	C34—C37	1.44 (3)
C1—C21	1.51 (2)	C37—N	1.11 (3)
C2—C31	1.49 (2)		
C2—C1—C3	58.5 (9)	C1—C2—C31	118.6 (12)
C1—C2—C3	59.8 (9)	C1—C2—C41	119.3 (12)
C1—C3—C2	61.8 (9)	C3—C2—C31	118.9 (12)
C2—C1—C11	119.1 (12)	C3—C2—C41	117.2 (12)
C2—C1—C21	116.6 (12)	C31—C2—C41	113.3 (12)
C3—C1—C11	118.5 (12)	C34—C37—N	174 (2)
C3—C1—C21	116.1 (12)	C14—O—C17	122 (2)
C11—C1—C21	115.8 (12)		

electron density is reduced in a bonding orbital, and strengthen the distal bond because of loss of electron density from an antibonding orbital. Alternatively, as discussed by Jason & Ibers (1977), the transfer of π -electron density from the substituent to the cyclopropane ring causes an increase in antibonding character of vicinal C—C bonds and an increase in bonding character of the distal C—C bond. Thus both processes result in the lengthening of C—C bonds vicinal to the substituent and shortening of the distal C—C bond across from the substituent. In the case of compounds (I)–(III), which have phenyl substituents bonded to two C atoms of the cyclopropane ring, the net effect is a very long C1—C2 bond and C1—C3 and C2—C3 bonds which are essentially unchanged from those normally found in cyclopropane, since the increase in bond length from an adjacent substituent is cancelled out by the decrease

caused by the substituent on the C atom opposite the bond.

The long C1—C2 bond in each compound is consistent with the explanation that there is π -electron conjugation between the phenyl rings and the cyclopropane ring. As discussed below, it is most likely that the major contribution to the conjugation is produced by π -electron donation from the phenyl

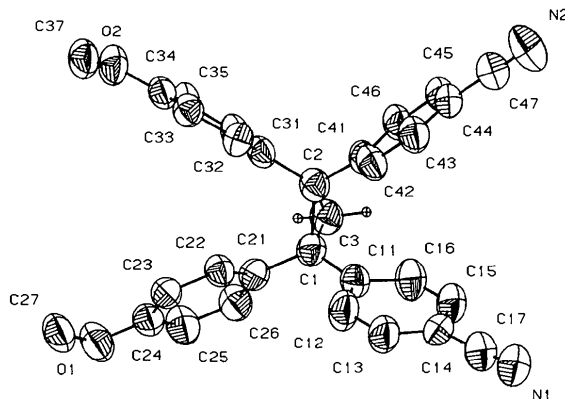


Fig. 1. The structure of (I) showing the atom numbering. H atoms have been omitted for clarity.

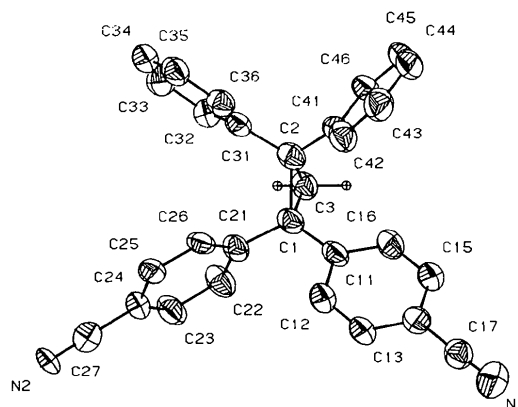


Fig. 2. The structure of (II).

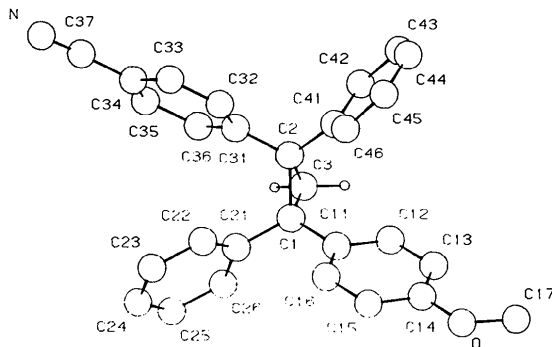


Fig. 3. The structure of (III).

groups to the cyclopropane ring rather than the more commonly proposed explanation of π -electron donation by the cyclopropane ring.

Explanations of the possible bonding interactions within cyclopropane and between the cyclopropane ring and substituents capable of π interactions have been given in detail previously (Walsh, 1949; Lauher & Ibers, 1975; Jason & Ibers, 1977). Essentially, interaction by donation of π electrons from the cyclopropane ring to the substituent requires the substituent to adopt the 'bisecting' position, that is, with the plane of the substituent's π system perpendicular to the distal C—C bond of the cyclopropane ring. In the 'perpendicular' orientation, where there is no overlap of the orbitals required for π donation to the substituent, the plane of the substituent's π system is parallel to the distal C—C bond. However, in cases where the substituent can donate π electrons to the cyclopropane ring, either the 'bisecting' or 'perpendicular' orientation is allowed depending on the orbitals involved. The angle θ has been used to describe the orientation of the π orbitals of the substituents (Jason & Ibers, 1977) and is defined as the acute angle between the normal to the plane of the substituent's π system and the C—C vector of the distal bond of the cyclopropane ring. Thus $\theta = 0^\circ$ corresponds to the 'bisecting' position, which should be the most favorable if the bonding involves π -electron donation to the substituent.

Table 5 lists the θ angles found for each of the phenyl substituents in the compounds (I)–(III). It is interesting to note that in each case one phenyl substituent on each C atom adopts almost exactly the 'perpendicular' conformation while the other adopts positions ranging from $\theta = 16$ – 61° . There does not appear to be any pattern as to whether cyanophenyl, methoxyphenyl or unsubstituted phenyl substituents prefer the 'perpendicular' position, although in (III) both the unsubstituted phenyl rings are involved. Although it was originally believed that the phenyl substituents would be π -electron acceptors and therefore require the 'bisecting' conformation, these results are not unusual. It has been demonstrated (Lauher & Ibers, 1975; Jason & Ibers, 1977) that many phenyl-substituted cyclopropanes do not adopt the preferred 'bisecting' conformation required for the explanation of conjugation *via* π -electron donation from the cyclopropane to the phenyl substituent. Such a description works well for compounds such as 1,1,2,2-tetracyanocyclopropane where there is no geometrical restriction on the orientation of the ligands and the π orbitals of the ligand can be correctly oriented to interact with the appropriate Walsh orbital of the cyclopropane ring. However, in the case of phenyl substituents, steric factors may also influence the orientation of the π system of each ring. This is

Table 5. The angle, θ ($^\circ$), between the phenyl ring planes and the C2—C3 vector

Ring No.	Atom Nos.	(I)	(II)	(III)
1	C11—C16	35.2	16.2	29.2
2	C21—C26	80.2	86.1	86.1
3	C31—C36	61.3	46.5	41.5
4	C41—C46	85.4	89.6	89.8

particularly so when two phenyl substituents are attached to the same C atom. Steric interactions would make it very difficult for both rings to adopt the 'bisecting' configuration.

The cyclopropane bond-length trends observed for (I), (II) and (III) can, however, be explained in terms of π donation to the cyclopropane ring, since one of the phenyl groups attached to each C atom adopts the 'perpendicular' conformation. It is uncertain how the other phenyl groups are involved in the bonding process since they do not appear to adopt a particular orientation and have a wide range of values for θ which does not put them in either the 'bisecting' or 'perpendicular' orientation. Steric effects may play a part here in preventing the second substituent from adopting the position in which orbital interactions are maximized. However, there is no indication that any phenyl group is any more or less involved in conjugation with a cyclopropane ring than any other phenyl group since there is no significant trend in the variation in the length of the C—C bonds between the cyclopropane rings and the phenyl groups.

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References

- AHMED, F. R. & GABE, E. J. (1964). *Acta Cryst.* **17**, 603–608.
 ALLEN, F. H. (1980). *Acta Cryst.* **B36**, 81–96.
 ALLEN, F. H. (1981). *Acta Cryst.* **B37**, 890–900.
 ARNOLD, D. R., WAYNER, D. D. M. & YOSHIDA, M. (1982). *Can. J. Chem.* **60**, 2313–2320.
 BASTIENSEN, O., FRITSCH, F. N. & HEDBERG, K. (1964). *Acta Cryst.* **17**, 538–543.
 CAMERON, T. S. & CORDES, R. E. (1979). *Acta Cryst.* **B35**, 748–750.
 DECLERQ, J. P., PIRET, P. & VAN MEERSSCHE, M. (1972). *Acta Cryst.* **B28**, 328–330.
 DELACY, T. P. & KENNARD, C. H. L. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 2141–2147.
 FRITCHIE, C. J. JR (1966). *Acta Cryst.* **20**, 27–36.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 HOFFMAN, R. (1970). *Tetrahedron Lett.* pp. 2907–2909.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 JASON, M. E. & IBERS, J. A. (1977). *J. Am. Chem. Soc.* **99**, 6012–6021.
 LAUHER, J. W. & IBERS, J. A. (1975). *J. Am. Chem. Soc.* **97**, 561–567.

- LEMLEY, J. T., SKARSTAD, P. M. & HUGHES, R. E. (1976). *Acta Cryst.* B32, 35–40.
- LONG, R. E., MADDOX, H. & TRUEBLOOD, K. N. (1969). *Acta Cryst.* B25, 2083–2094.
- MEUNIER-PIRET, J. & VAN MEERSSCHE, M. (1971). *Bull. Soc. Chim. Belg.* 80, 475–479.
- PERRETTA, A. T. & LAURIE, V. W. (1975). *J. Chem. Phys.* 62, 2469–2473.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- WALSH, A. (1949). *Trans. Faraday Soc.* 45, 179–190.
- WANG, Y. & STUCKY, G. D. (1973). *Acta Cryst.* B29, 1255–1258.

Acta Cryst. (1990). C46, 2115–2117

Structure of 5-[(1*S*,2*S*)-2-Chlorocyclopropyl]-1-(2-deoxy- β -D-ribofuranosyl)-uracil

BY STEVEN C. MOSIMANN, BERNARD D. SANTARSIERO AND MICHAEL N. G. JAMES

Department of Biochemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2HY

AND MANJU TANDON, LEONARD I. WIEBE AND EDWARD E. KNAUS

Faculty of Pharmacy and Pharmaceutical Sciences, University of Alberta, Edmonton, Alberta, Canada T6G 2N8

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Abstract. C₁₂H₁₅ClN₂O₅, $M_r = 302.72$, monoclinic, $P2_1$, $a = 5.0406$ (5), $b = 16.363$ (3), $c = 7.962$ (2) Å, $\beta = 90.66$ (1)°, $V = 656.6$ (2) Å³, $Z = 2$, $D_x = 1.531$ g cm⁻³, $\lambda(\text{Cu } K\alpha_1) = 1.54051$ Å, $\mu = 73.1$ cm⁻¹, $F(000) = 316$, $T = 293$ K, $R = 0.028$ for 2046 unique reflections. The absolute configuration about C(7) and C(9) of the cyclopropane ring is *S*. The 5'-substituted pyrimidine is *anti* with respect to the deoxyribose, which is in the 2'-*endo* puckering mode. The torsion angle about C(4')—C(5') is *gauche-gauche*.

Introduction. Olefinic 5-substituted-2'-deoxyuridines are potent and selective antiviral agents against herpes simplex virus type 1 (HSV-1) (De Clerq, Descamp, De Somer, Barr, Jones & Walker, 1979; Goodchild, Porter, Raper, Sims, Upton, Vitney & Wadsworth, 1983). Here we report on the crystal and molecular structure of a 5-chlorocyclopropyl derivative of 2'-deoxyuridine as part of a program to evaluate the antiviral activity of such compounds.

Experimental. The title compound was recrystallized from methanol:chloroform [3:1(v/v)] as translucent rods. The space group was determined by systematic absences on a precession film and on diffractometer-collected intensity data. Least-squares refinement of 25 high-angle reflections [$43 \leq 2\theta \leq 119^\circ$], constrained to a monoclinic cell, yielded unit-cell parameters. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using Ni-filtered Cu $K\alpha$ radiation. Background corrections were

based on $\omega/2\theta$ scans. The crystal dimensions were $0.7 \times 0.2 \times 0.2$ mm.

A hemisphere of data ($0 \leq h \leq 5$, $-18 \leq k \leq 18$, $-8 \leq l \leq 8$) corresponding to $1.5 < \theta < 60^\circ$ was collected. The resulting 2184 reflections yield an R_M of 0.023 ($R_M = \sum |I - \langle I \rangle| / \sum I$), 1092 reflections) when Friedel equivalent reflections are averaged. To preserve anomalous-scattering information, only the $0kl$'s of the 2184 reflections were averaged to give 1926 reflections, $R_M = 0.025$. These measurements were considered observed and included in the subsequent refinement. Empirical absorption, Lorentz and polarization factors were applied. The maximum and minimum transmission factors were 1.000 and 0.917. Four check reflections (053, 080, 212 and 222) were collected every 4 h of exposure time and no significant variation in intensity was observed. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974). All calculations were carried out using XTAL2.4 (Hall & Stewart, 1987), ORTEPII (Johnson, 1976) and PLUTO (Motherwell & Clegg, 1978).

The single chlorine position was determined from a Patterson map, and was used to generate a preliminary F_{obs} map ($R = 0.572$). Since this resulted in the superimposition of each enantiomer, the non-H atoms of the cyclopropane ring were introduced with idealized coordinates prior to generating a second F_{obs} map ($R = 0.592$). By breaking the symmetry of the previous map, the non-H atoms of the six-membered ring were located. At this point, an F_{obs} map ($R = 0.529$) was generated using modified coord-