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The Structure of PO-Substituted Norcaradienes. II. The Crystal and Molecular Structures of Dimethyl 2,5-Dichloro-7-phenylnorcaradiene-7-phosphonate and Dimethyl 2,5-Dibromo-7-phenylnorcaradiene-7-phosphonate

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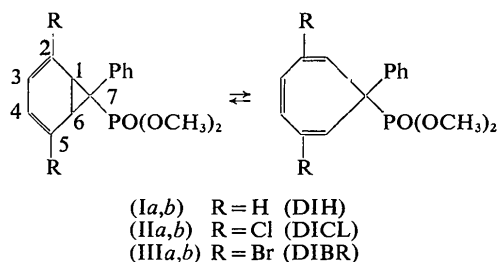
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The structures of two 2,5-halogeno-substituted norcaradienes have been determined from single-crystal X-ray diffraction data. Dimethyl 2,5-dichloro-7-phenylnorcaradiene-7-phosphonate (DICL) is triclinic, space group $P\bar{1}$, with $a = 11.048$ (3), $b = 8.171$ (5), $c = 8.874$ (3) Å, $\alpha = 96.80$ (4), $\beta = 96.49$ (3), $\gamma = 95.94$ (4)°, $Z = 2$. Dimethyl 2,5-dibromo-7-phenylnorcaradiene-7-phosphonate (DIBR) is monoclinic, $P2_1/b$, with $a = 9.033$ (2), $b = 21.247$ (8), $c = 8.771$ (2) Å, $\gamma = 92.81$ (2)°, $Z = 4$. Both structures were solved by Patterson methods and refined by full-matrix least-squares calculations. The final R for DICL was 0.038 for 1889 observed reflexions and for DIBR 0.057 (1187 reflexions). The molecular geometries are very similar: an *endo* phenyl ring, a distortion of the tetrahedral configuration around the phosphorus atom, and a nearly regular cyclopropane ring. An important difference between the structures concerns the cyclohexadiene ring: it is folded along the axis C(2)–C(5) at an angle of 4.8° for DICL and 2.9° for DIBR. This increase of planarity may be related to the greater stability of the bromo-substituted norcaradiene.

Introduction

The valence tautomerism between norcaradiene and cycloheptatriene can be influenced by several steric



and electronic factors depending on the nature of the substituents. In a previous paper, we have reported the structure of (Ia) (Maas, Fischer & Regitz, 1974). In this molecule, stabilization of the norcaradiene skeleton can only be explained by electronic and steric interaction of the C(7) substituents with the molecular orbitals of the cyclopropane ring and perhaps with the diene system. Substitution of H by halogens in the cyclohexadiene ring (II and III) causes an increasing stabilization of the bicyclic form, as observed from the temperature dependence of their ^1H n.m.r. spectra (Günther, Tunggal, Regitz, Scherer & Keller, 1971): in solution, the spectrum of (I) changes with temperature in a manner typical for a fast, dynamic equilibrium between the valency tautomers (Ia) and (Ib). DICL shows only small changes and the spectrum of DIBR is completely temperature-independent between -100°

and $+40^\circ\text{C}$. Structure analysis of DICL and DIBR might reveal significant differences between the structures which could explain the increased stability of the bicyclic form.

Experimental

DICL was prepared by the method given by Scherer, Hartmann, Regitz, Tunggal & Günther (1972). DIBR was synthesized by photolysis (Philips HPK 125 high-pressure mercury lamp, Pyrex filter, 24 h) of dimethyl phenyldiazomethanephosphonate in molten 1,4-dibromobenzene at 105°C . The reaction mixture was dissolved in benzene and chromatographed over silica gel; *p*-dibromobenzene was eluted with benzene; elution with ethyl acetate gave DIBR in 13% yield. [$\text{C}_{15}\text{H}_{15}\text{Br}_2\text{O}_3\text{P}$: C, 41.6; H, 3.48%. Found: C, 41.1; H, 3.63%. ^1H n.m.r. spectrum ($\delta_{\text{CDCl}_3}^{\text{TMS}}$, p.p.m.): 3.30 (*d*, $^3J_{\text{P,H}} = 16.5$ Hz); 3.76 (*d*, $^3J_{\text{P,CH}_3} = 10.4$ Hz); 5.86 (*s*); 7.28 (*m*). Infrared spectrum (cm^{-1}): 1248 (P=O); 1057, 1026, 1015 (P–O–C)].

Both compounds were recrystallized from ether at -5°C ; two single crystals with prismatic shape and dimensions $0.17 \times 0.18 \times 0.39$ mm (DICL) and $0.430 \times 0.060 \times 0.156$ mm (DIBR) were selected for the diffraction experiments. Preliminary information on lattice constants and space group were obtained from precession and DeJong–Bouman photographs. From systematic extinctions, the monoclinic space group $P2_1/b$ (C_{2h}^2 , No. 14, 1st setting) could be deduced for DIBR, whereas no systematic absences indicated the triclinic system for DICL; at a later stage, a statistical test confirmed space group $P\bar{1}$ (No. 2). For all subsequent ex-

perimental work, the crystals were mounted on a Siemens automatic single-crystal diffractometer with [001] parallel to the ϕ direction of the goniometer. θ values of 29 reflexions between 19.5 and 23.5° (Mo $K\alpha$) for DICL and 35 with $16.6^\circ \leq \theta \leq 21.5^\circ$ for DIBR were determined; lattice constants were obtained by a least-squares fit (Burnham, 1961).

Crystal data

	DICL	DIBR
Formula	$C_{15}H_{15}Cl_2O_3P$	$C_{15}H_{15}Br_2O_3P$
F.W.	345.2	434.1
Space-group	none	$hk0, k$ odd
extinctions		$00l, l$ odd
Space group	$P\bar{1}$	$P2_1/b$
Unit cell	$a=11.048$ (3) Å $b=8.171$ (5) $c=8.874$ (3) $\alpha=96.80$ (4) $^\circ$ $\beta=96.49$ (3) $\gamma=95.94$ (3)	$a=9.033$ (2) Å $b=21.247$ (8) $c=8.773$ (2) $\gamma=92.81$ (2) $^\circ$
V_c	785.7 (4) Å ³	1681.4 (6) Å ³
Z	2	4
D_m	1.44 g cm ⁻³	1.698 g cm ⁻³
D_c	1.46	1.714
$F(000)$	356	856
$\mu(\text{Mo } K\alpha)$	4.86 cm ⁻¹	51.77 cm ⁻¹

Intensity data were collected with Nb-filtered Mo $K\alpha$ radiation, a scintillation counter and a pulse-height analyser.

DICL

With the moving-crystal stationary-counter technique and differential step scanning, 2775 reflexions

with $0^\circ < \theta \leq 25.00^\circ$ were measured. Some 450 low-angle reflexions, most of which were very strong, were remeasured at reduced power and given a second scale factor. After every 50 reflexions, a standard reflexion was measured (053); its intensity differed by $\pm 1.5\%$ over the whole measuring time. The background for each reflexion was approximated by a straight line calculated from background points at each side of the reflexion, the number of points varying with the peak-to-background ratio (Klar, 1967). 97 reflexions were removed from the data set because their intensity profile was apparently in error; all reflexions with $\theta \leq 2^\circ$ belonged to this group. After correction for Lorentz and polarization effects, all reflexions with $F_{\text{obs}} < 5\sigma(F)$ were treated as unobserved. Only the remaining 1889 reflexions were used for further calculations. No absorption correction was applied.

DIBR

2110 independent reflexions in the range $0^\circ < \theta \leq 22.25^\circ$ were measured with the θ - 2θ -scan technique and the built-in 'five-values' method. The scan range was $1.22^\circ + \Delta K\alpha$ ($\Delta K\alpha = \theta_{K\alpha 2} - \theta_{K\alpha 1}$). A linear decrease of intensity due to crystal decomposition was indicated by a standard reflexion ($\bar{3}20$), which was monitored after every 50 reflexions. At the end it had lost 11% of its original intensity. Thus, all reflexions were re-scaled according to the accumulated X-ray exposure time. After the Lp-correction, standard deviations $\sigma(I)$ were derived from counting statistics and converted to $\sigma(F)$. All reflexions with $F_{\text{obs}} < 4\sigma(F)$ were considered unobserved. Structure solution and refinement was performed with the remaining 1188 reflexions. An absorption correction was introduced during the refinement.

Table 1. Atomic parameters of the non-hydrogen atoms of DICL

Standard deviations are in parentheses. All parameters are multiplied by 10^4 . The temperature factor expression is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \dots + 2U_{23}klb^*c^*)]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	3400 (1)	7546 (1)	4094 (1)	554 (5)	441 (5)	565 (6)	53 (4)	24 (4)	-32 (4)
Cl(2)	5627 (1)	1130 (2)	1814 (1)	638 (7)	934 (9)	778 (8)	369 (6)	39 (6)	-278 (7)
P	1407 (1)	1736 (1)	3248 (1)	403 (5)	349 (5)	294 (4)	22 (4)	58 (3)	71 (3)
O(1)	479 (2)	3037 (3)	3523 (3)	475 (14)	447 (14)	615 (16)	76 (11)	265 (13)	171 (12)
O(2)	681 (2)	542 (3)	1857 (3)	500 (14)	431 (14)	426 (14)	-9 (11)	-53 (11)	68 (11)
O(3)	1834 (3)	943 (3)	4565 (3)	644 (17)	506 (15)	348 (13)	22 (13)	39 (12)	143 (11)
C(1)	3381 (3)	4214 (4)	3764 (4)	385 (18)	434 (19)	252 (16)	44 (14)	28 (14)	11 (13)
C(2)	3934 (3)	5746 (4)	3325 (4)	361 (18)	467 (20)	341 (18)	4 (15)	-19 (15)	-18 (15)
C(3)	4789 (3)	5813 (5)	2401 (4)	373 (19)	628 (25)	480 (21)	-71 (18)	29 (17)	54 (19)
C(4)	5307 (4)	4319 (6)	1869 (5)	319 (20)	901 (35)	472 (23)	-9 (20)	77 (18)	-43 (22)
C(5)	4922 (3)	2878 (5)	2286 (4)	337 (19)	691 (26)	403 (20)	142 (18)	-10 (15)	-132 (19)
C(6)	3904 (3)	2644 (5)	3191 (4)	379 (19)	506 (21)	348 (18)	116 (16)	5 (14)	18 (16)
C(7)	2616 (3)	2931 (4)	2533 (3)	319 (17)	385 (17)	275 (16)	53 (13)	29 (13)	46 (13)
C(8)	-660 (5)	2537 (8)	4089 (7)	560 (28)	717 (33)	840 (36)	80 (24)	372 (28)	310 (29)
C(9)	1033 (5)	-1073 (5)	1422 (6)	698 (33)	408 (23)	650 (29)	36 (21)	-77 (25)	-78 (21)
C(10)	2342 (3)	3269 (4)	921 (3)	259 (15)	408 (18)	275 (16)	0 (13)	58 (12)	36 (13)
C(11)	1754 (3)	4617 (5)	594 (4)	313 (17)	424 (19)	344 (18)	31 (14)	58 (14)	43 (15)
C(12)	1411 (3)	4849 (5)	-912 (4)	391 (19)	529 (22)	395 (21)	40 (17)	29 (15)	136 (17)
C(13)	1657 (3)	3734 (5)	-2089 (4)	421 (20)	694 (26)	283 (18)	-58 (18)	5 (15)	136 (18)
C(14)	2248 (3)	2390 (5)	-1785 (4)	451 (21)	592 (23)	279 (18)	-53 (18)	77 (15)	-21 (17)
C(15)	2597 (3)	2167 (5)	-284 (4)	415 (19)	398 (19)	337 (18)	36 (16)	72 (15)	11 (15)

Solution and refinement of the structures

Both structures were solved from Patterson syntheses. Refinement was by full-matrix least-squares calculations with the program *SBLQ* (Onken, 1967). Because of core limitation, the parameters were divided into two blocks which were refined consecutively. The first block contained the atoms in the phenyl ring, the phosphonate group and C(7), the second all other atoms and also C(7) as the connexion point of the blocks. The scattering factors were those of Onken & Fischer (1968). The reliability indices are defined as $R = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_w = (\sum w \Delta^2 F / \sum w F_o^2)^{1/2}$. The weight w was taken as $w = (a + bF_o + cF_o^2)^{-1}$.

All calculations were performed on a CDC 3300 computer at the Universität des Saarlandes.

DICL

From a sharpened Patterson synthesis (Stout & Jensen, 1970), the positions of the three heavy atoms were found. A Fourier synthesis enabled us to assign the three heavy atoms unambiguously. After a second Fourier synthesis, all atoms except hydrogens were located. In the first four cycles of isotropic refinement, we varied alternately scale and temperature factors (besides the positional parameters, which always were allowed to vary) and multiplied all shifts by 0.5. Two further isotropic cycles with variation of all parameters reduced R to 0.125. The coefficients used in the weighting formula were $a = 3.60$, $b = 0.0028$, $c = 0.000054$. The refinement was continued anisotropically and gave $R = 0.057$, $R_w = 0.065$. A difference synthesis revealed all hydrogen atoms. Their heights were $0.26\text{--}0.33 \text{ e } \text{Å}^{-3}$ for the methyl H's and $0.41\text{--}0.56 \text{ e } \text{Å}^{-3}$ for all others. After three further cycles, in which the hydrogens were included with isotropic temperature factors, refine-

ment converged at $R = 0.038$ and $R_w = 0.043$. The error of fit, $[\sum w \Delta^2 F / (m - n)]^{1/2}$, was 6.39 ($m = 1889$, $n = 249$). A final difference synthesis was nearly featureless, with peak heights $< 0.26 \text{ e } \text{Å}^{-3}$. There was some evidence for residual electron density outside the cyclopropane ring bonds. This phenomenon has been reported for similar compounds and has been accounted for by bent bonds (Hartman & Hirshfeld, 1966; Fritchie, 1966). The final positional and thermal parameters are given in Tables 1 and 2.

Table 2. Final atomic parameters of the hydrogen atoms of DICL

All positional parameters are multiplied by 10^3 ; standard deviations are in parentheses.

	x/a	y/b	z/c	$B(\text{Å}^2)$
H(1)	309 (3)	430 (5)	478 (4)	2.0 (8)
H(2)	515 (3)	682 (5)	204 (4)	1.6 (7)
H(3)	591 (3)	440 (5)	133 (4)	1.8 (8)
H(4)	396 (4)	185 (5)	376 (4)	2.0 (8)
H(5)	-62 (4)	163 (6)	461 (5)	3.4 (1.0)
H(6)	-94 (6)	351 (9)	448 (8)	7.4 (1.7)
H(7)	-121 (7)	217 (10)	317 (9)	8.9 (2.0)
H(8)	-45 (5)	-162 (6)	81 (6)	4.2 (1.1)
H(9)	191 (5)	-99 (6)	132 (6)	4.1 (1.1)
H(10)	123 (6)	-175 (8)	221 (7)	7.4 (1.6)
H(11)	155 (3)	533 (4)	140 (4)	1.2 (7)
H(12)	94 (3)	577 (4)	-108 (4)	1.2 (7)
H(13)	141 (4)	396 (5)	-303 (4)	2.5 (8)
H(14)	240 (3)	163 (4)	-258 (4)	1.7 (8)
H(15)	299 (2)	121 (3)	-7 (28)	1.5 (7)

DIBR

The positions of the phosphorus and the two bromine atoms were found from a Patterson synthesis and stereochemical considerations. After two Fourier syntheses, all non-hydrogen atoms were located. The same weighting scheme was used with coefficients chosen to

Table 3. Final atomic parameters of DIBR

E.s.d.'s are in parentheses. All parameters are multiplied by 10^4 . The anisotropic temperature factor is given by $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \dots + 2U_{23}klb^*c^*)]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	-2364 (2)	1185 (1)	3371 (2)	495 (10)	1198 (16)	951 (15)	97 (9)	124 (9)	-244 (11)
Br(2)	3093 (2)	-436 (1)	744 (2)	693 (10)	655 (11)	827 (13)	106 (7)	-4 (9)	-207 (9)
P	2571 (4)	1935 (2)	1132 (4)	602 (22)	429 (21)	312 (21)	-87 (17)	44 (17)	-0 (18)
O(1)	4247 (10)	1801 (4)	1003 (12)	652 (64)	588 (59)	955 (83)	-106 (49)	333 (59)	56 (59)
O(2)	2593 (10)	2478 (4)	2299 (10)	812 (64)	452 (55)	581 (63)	10 (48)	-64 (52)	-113 (49)
O(3)	1815 (12)	2051 (4)	-281 (10)	1270 (88)	610 (64)	324 (57)	-203 (57)	-72 (58)	28 (48)
C(1)	1537 (12)	681 (6)	1003 (14)	425 (70)	610 (84)	409 (81)	-68 (59)	-128 (65)	-66 (74)
C(2)	1587 (13)	28 (5)	1578 (13)	499 (71)	271 (75)	370 (71)	-87 (57)	8 (64)	-47 (61)
C(3)	670 (14)	-215 (6)	2630 (18)	487 (79)	497 (82)	838 (120)	-164 (68)	-72 (82)	-84 (85)
C(4)	-537 (15)	145 (7)	3229 (18)	627 (90)	655 (100)	663 (114)	-338 (77)	-12 (81)	-56 (89)
C(5)	-733 (12)	727 (7)	2738 (17)	280 (66)	633 (103)	756 (109)	-164 (66)	0 (69)	-56 (89)
C(6)	254 (12)	1069 (6)	1612 (14)	433 (70)	655 (89)	363 (72)	-19 (65)	-128 (61)	-75 (71)
C(7)	1846 (12)	1248 (5)	2093 (12)	437 (70)	407 (75)	250 (71)	-0 (58)	36 (57)	19 (59)
C(8)	5290 (19)	2241 (8)	340 (25)	833 (120)	994 (139)	1661 (200)	-135 (104)	646 (129)	375 (140)
C(9)	1253 (20)	2845 (8)	2540 (24)	1126 (139)	859 (130)	1353 (172)	589 (113)	-176 (130)	-9 (124)
C(10)	2386 (12)	1150 (5)	3702 (12)	342 (69)	429 (73)	246 (71)	-125 (57)	0 (55)	9 (59)
C(11)	1680 (12)	1444 (6)	4906 (15)	280 (64)	520 (84)	515 (88)	-77 (57)	116 (66)	-9 (72)
C(12)	2241 (14)	1398 (6)	6409 (14)	520 (81)	791 (98)	289 (82)	-145 (72)	-0 (65)	-38 (74)
C(13)	3507 (14)	1075 (6)	6703 (16)	499 (82)	475 (87)	472 (91)	-77 (67)	24 (73)	9 (75)
C(14)	4198 (14)	808 (6)	5483 (17)	437 (78)	701 (100)	655 (109)	87 (71)	-116 (77)	28 (85)
C(15)	3659 (13)	833 (6)	3990 (14)	392 (68)	520 (82)	382 (82)	-87 (70)	16 (62)	-122 (68)

make ΔF independent of F_o . Their final values were $a=3.78$, $b=-0.0495$, $c=0.000359$. In the first stage of isotropic refinement, the strongest reflexion (200) was discarded, because it was obviously in error. After isotropic and anisotropic refinement, convergence was reached at $R=0.069$ and $R_w=0.079$. A difference map showed peaks at all positions except for hydrogens. They were included in the refinement with $B=5.0 \text{ \AA}^2$. Their parameter shifts were set to zero if they appeared to be unreasonably high. After three cycles, refinement ended with $R=0.065$. At this point, an absorption correction was introduced (Wehe, Busing & Levy, 1962). Two final cycles of anisotropic refinement (with all hydrogen parameters kept constant) led to $R=0.057$ and $R_w=0.062$. All shifts were less than 0.8σ ; the sum $\sum w\Delta^2 F$ was reduced by 1% in the last cycle. The error of fit was still 6.63. The final parameters are given in Tables 3 and 4; the standard deviations are estimated from the inverse matrix.*

Table 4. Positional parameters (multiplied by 10^3) of hydrogen atoms of DIBR

E.s.d.'s have not been evaluated.

	z/a	y/b	z/c
H(1)	182	78	-23
H(2)	95	-66	297
H(3)	-124	-13	403
H(4)	-26	132	56
H(5)	70	260	332
H(6)	155	328	276
H(7)	63	297	152
H(8)	630	213	84
H(9)	535	260	77
H(10)	583	215	-27
H(11)	81	170	469
H(12)	164	169	722
H(13)	399	103	773
H(14)	569	58	571
H(15)	402	61	316

Description and discussion of the structures

Bond lengths and angles are given in Figs. 1 and 2 for DICL and Figs. 3 and 4 for DIBR. Fig. 5 shows the DICL molecule (Johnson, 1965), the thermal ellipsoids corresponding to 50% probability. The bond lengths involving hydrogen atoms are given in Table 5 for both structures.

The results for DIBR have larger error, but the structural features of both compounds are similar to each other and to (Ia) (DIH).

The phenyl rings are *endo* with respect to the six-membered diene ring. This had been expected from the magnitude of the coupling constant $^3J_{P,H}$ in the ^1H n.m.r. spectrum (Scherer *et al.*, 1972). The aromatic

* Tables of observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30576 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

rings take the energetically most favoured conformation, *i.e.* they are bisected by a mirror plane defined by the atoms C(7), P and the midpoints of the bonds C(1)-C(6) and C(3)-C(4). Consequently, the π -orbital of C(10) lies orthogonal to the molecular orbitals in the cyclopropane ring, and no electronic interaction between them [according to the model proposed by Hoffmann (1970) and Günther (1970)] can take place. Thus, we have confirmed a suggestion of Günther, Peters & Wehner (1973), who have found no significant influence of *para*-substitution in the *endo* phenyl ring on the norcaradiene-cycloheptatriene equilibrium. A π -type interaction of cyclopropane molecular orbitals with neighbouring π -acceptors can, therefore,

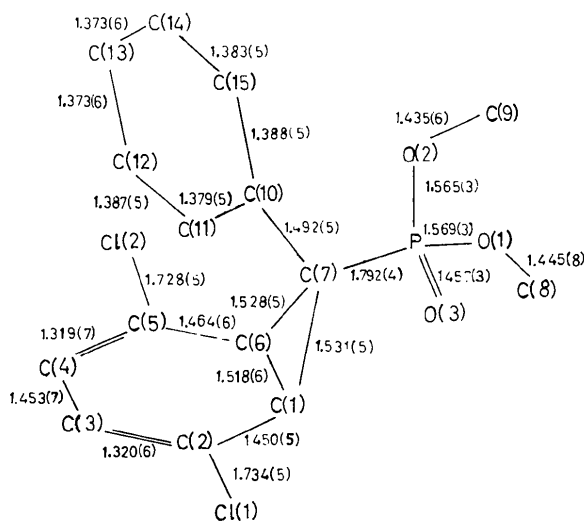


Fig. 1. Bond distances (Å) in DICL.

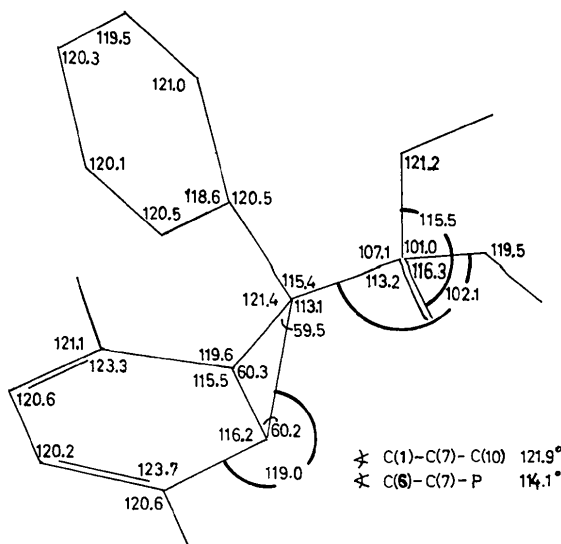


Fig. 2. Bond angles ($^\circ$) in DICL. Standard deviations are 0.2-0.3 $^\circ$ for angles involving P or Cl, and 0.3-0.5 $^\circ$ for all others.

only arise from the *exo* phosphoryl group. In the crystal, however, this conjugation cannot be ideal, because the P=O linkage does not lie in the plane bisecting the cyclopropane ring and passing through C(7), but is turned out of it by 20.5° in D1CL and 10.7° in D1BR. Because this acceptor function of the phosphoryl group is not very strong, one would expect that the bond C(1)–C(6) is not shortened by the same amount as that in 2,5-dimethyl-7,7-dicyanonorcaradiene (1.501 Å) where two π -electron acceptors are present at C(7) (Fritchie, 1966). Indeed, the following cyclopropane bond lengths C(1)–C(6), C(1)–C(7), C(6)–C(7) are

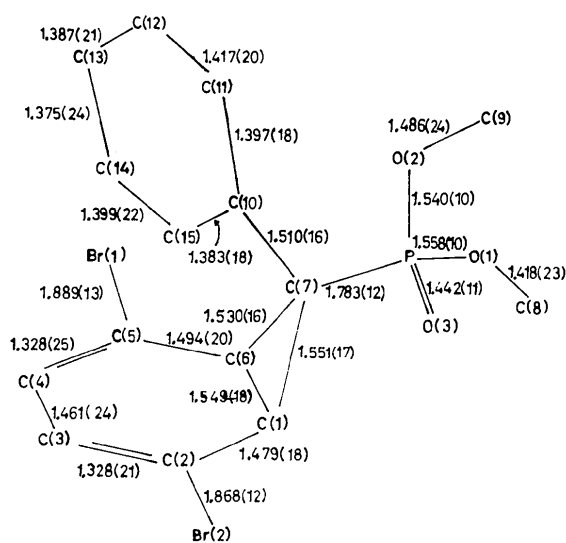


Fig. 3. Bond distances (Å) in D1BR.

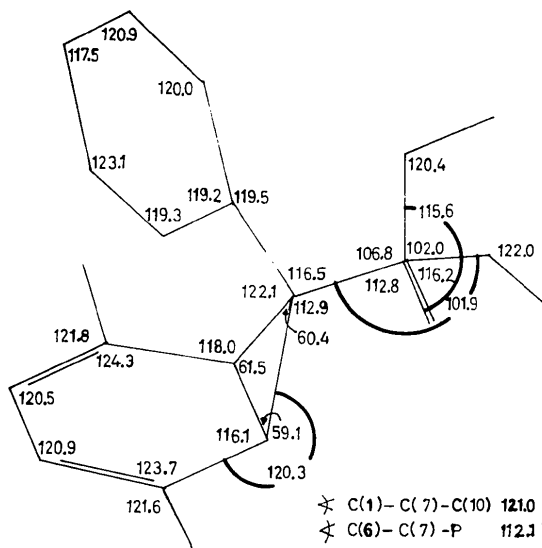


Fig. 4. Bond angles (°) in D1BR. E.s.d.'s are 1.1° for P–O–C, 0.6–0.8° for all other angles involving P, 1.0° for C–C–Br, 0.8–1.4° for C–C–C.

found: 1.518 (6), 1.531 (5), 1.528 (5) Å in D1CL, and 1.549 (18), 1.551 (17), 1.530 (16) Å in D1BR. Thus, the difference between the C(1)–C(6) bond and C(1)–C(7), C(6)–C(7) bonds nearly equals the sum of the e.s.d.'s for D1CL. In D1BR, the corresponding difference is within the standard deviations. In any case, the bonds are longer than in cyclopropane itself (1.510 ± 0.002 Å; Bastiansen, Fritsch & Hedberg, 1964). These relations have already been found in DIH, and we can conclude that the stabilization of the norcaradiene form caused by halogen substitution in the cyclohexadiene ring is not correlated with significant changes in the geometry of the three-membered ring.

Table 5. Bond distances involving hydrogen atoms (Å)

E.s.d.'s for D1BR have not been calculated. They are estimated to be about 0.15–0.20 Å.

	D1CL	D1BR
H(1)–C(1)	0.99 (4)	1.13
H(2)–C(3)	0.98 (4)	1.04
H(3)–C(4)	0.86 (5)	1.10
H(4)–C(6)	0.87 (5)	1.18
H(5)–C(8)	0.92 (6)	0.98
H(6)–C(8)	0.92 (9)	0.97
H(7)–C(8)	0.95 (9)	1.09
H(8)–C(9)	0.84 (6)	1.05
H(9)–C(9)	0.98 (7)	0.85
H(10)–C(9)	0.97 (8)	0.76
H(11)–C(11)	0.93 (4)	1.00
H(12)–C(12)	0.97 (4)	1.10
H(13)–C(13)	0.90 (5)	1.00
H(14)–C(14)	0.92 (5)	0.98
H(15)–C(15)	0.96 (4)	0.93

As in DIH, the six-membered diene ring in D1CL is not quite planar, but folded along the axis C(2)–C(5) at an angle of 4.8°, C(3) and C(4) lying towards the phenyl ring. The halogen atoms are displaced to the other side; the distances from the least-squares planes (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) defined by each half of the diene ring range from 0.125 to 0.177 Å (see Table 6). For D1BR, we find an analogous angle of 2.9°, but because of the high e.s.d.'s, this value is rather uncertain: the least-squares plane of the diene ring results in standard deviations of 0.017 Å for the atoms defining the plane; this is in the range of the positional errors (0.014 Å). Thus, we can conclude that the folding angle in D1BR is less than or equal to that in D1CL (see also Table 7). On comparing the magnitude of these dihedral angles with that found in other norcaradienes (Table 8), a correlation with the volume of the substituents at C(2) and C(5) is obvious: the angle α of $6.7 \pm 0.3^\circ$ [averaged for the unsubstituted norcaradienes DIH and spiro(indene-1,7'-norcaradiene)] is somewhat greater than in the norcaradienes bearing the larger groups CH₃ or Cl [$4.5 \pm 0.3^\circ$; both groups have a similar volume: 22.1 \AA^3 for the methyl group (Kitaigorodskii, 1957) and 23.5 \AA^3 for Cl].

From these observations, we suggest that the stabilization of the bicyclic skeleton by substituents on the

Table 6. *Some least-squares planes in DICL with deviations (Å) of atoms defining the plane and distances of some other atoms*

x, y, z are the axes of the triclinic unit cell.

(a) Phenyl ring

$$9.26224x + 3.72079y - 1.54468z = 3.24925$$

C(10)	-0.006	C(11)	0.001	C(12)	0.003
C(13)	-0.002	C(14)	-0.002	C(15)	0.006

(b) Plane C(2)-C(3)-C(4)-C(5)

$$6.68705x + 0.05332y + 6.24310z = 4.73553$$

C(2)	0.002	C(4)	0.003	Cl(1)	0.135
C(3)	-0.003	C(5)	-0.002	Cl(2)	0.165

(c) Plane C(2)-C(3)-C(6)-C(5)

$$6.11753x - 0.34110y + 6.70330z = 4.44239$$

C(2)	-0.003	C(6)	-0.005	Cl(1)	0.125
C(1)	0.005	C(5)	0.003	Cl(2)	0.177

Table 7. *Some least-squares planes in DIBR with deviations (Å) of atoms defining the planes and distances of Br atoms*

x, y, z refer to the monoclinic unit cell.

(a) Phenyl ring

$$4.67743x + 17.33608y - 1.31123z = 2.63404$$

C(10)	-0.010	C(11)	0.012	C(12)	-0.003
C(13)	-0.009	C(14)	0.011	C(15)	-0.002

(b) Plane C(2)-C(3)-C(4)-C(5)

$$5.31368x + 7.17240y + 6.32109z = 1.86200$$

C(2)	-0.001	C(4)	-0.002	Br(1)	-0.137
C(3)	0.002	C(5)	0.001	Br(2)	-0.062

(c) Plane C(2)-C(1)-C(6)-C(5)

$$5.17854x + 6.38692y + 6.58134z = 1.88279$$

C(2)	-0.004	C(6)	-0.008	Br(1)	-0.132
C(1)	0.008	C(5)	0.004	Br(2)	-0.071

Table 8. *Folding angles in some norcaradienes (Å)*

	α	β	Reference
Spiro (indene-1,7'-norcaradiene)	7.0	68.5	1
DIH	6.4	68.9	2
DICL	4.8	69.6	3
2,5-Dimethyl-7,7-dicyanonorcaradiene	4.2	71.9	4
DIBR	2.9	69.5	3

(1) Dreissig, Luger, Rewicki & Tuchscherer (1973). (2) Maas, Fischer & Regitz (1974). (3) This work. (4) Fritchie (1966).

diene ring is more steric than electronic in nature. Further support for our suggestion comes from a recent communication of Klärner (1974). By analysis of temperature-dependent n.m.r. spectra, he found the same stabilization effect of the bicyclic form in 7-methyl-7-cyanonorcaradienes/cycloheptatrienes which are substituted at C(2) either by methyl or bromine.

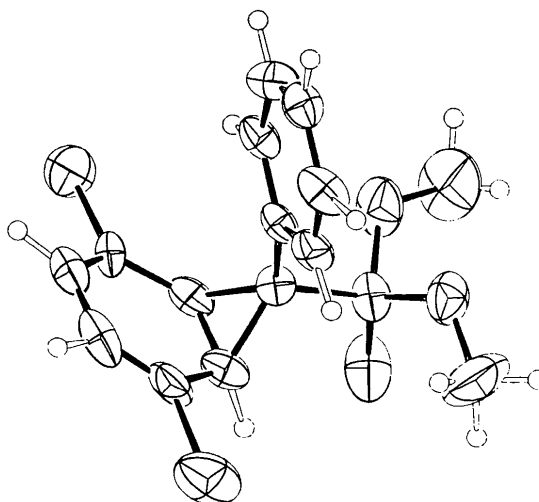


Fig. 5. Perspective view of DICL as drawn by ORTEP.

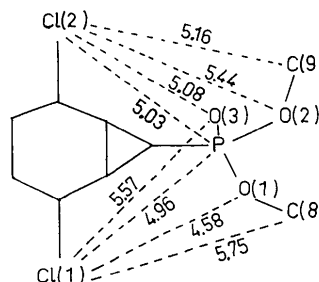


Fig. 6. Some intramolecular distances (Å) in DICL showing the deviations from the ideal C_3 -symmetry.

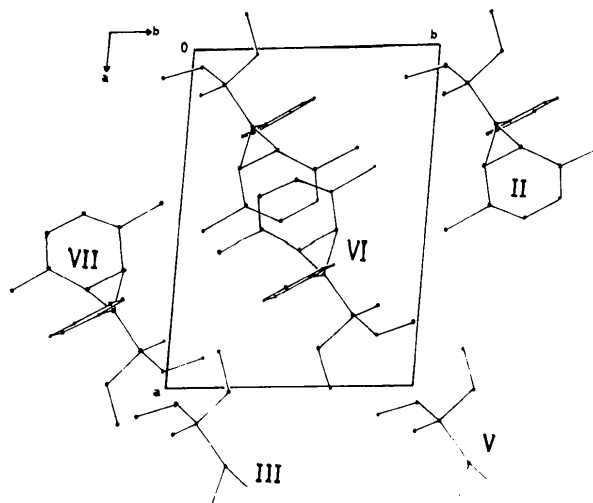


Fig. 7. Unit cell of DICL. The projection is normal to the ab plane. Symmetry code is as in Table 8.

The dihedral angle β between the cyclopropane ring and the plane C(1)–C(2)–C(5)–C(6) is $69.6 \pm 0.4^\circ$ in D1CL and $69.5 \pm 1.3^\circ$ in D1BR. Table 8 indicates no substantial variation for the norcaradienes analysed so far.

Some other features of both structures have already been observed for DIH: all bonds adjacent to the three-membered ring are shortened. This can be explained by the particular hybridization state of the cyclopropane C atoms (Bent, 1961). As in DIH, considerable deviations from the tetrahedral configuration around the P atom are observed in both compounds. The two ester groups are very regular in D1CL [P–O(1) = 1.569 (3), P–O(2) = 1.565 (3), O(1)–C(8) 1.445 (8) and O(2)–C(9) 1.435 (6) Å; P–O(1)–C(8) 119.5 (3), P–O(2)–C(9) 121.3 (3)°]. In D1BR however, the two (P)–O–C bonds lengths differ markedly [1.486 (24) vs. 1.418 (23) Å]. This difference may be caused by errors in the positions of the highly vibrating methyl–C atoms.

The dimensions in the phosphonate group fall in the expected range [see Corbridge (1971) and references cited therein]. As in DIH, the phosphonate group of D1CL and D1BR is not bisected by the 'mirror plane' passing through the other part of the molecule and defined by P, C(7) and the midpoints of C(1)–C(6) and C(3)–C(4). The appreciable deviations from the ideal C_s symmetry are shown in Fig. 6 for D1CL; they are similar in D1BR and probably caused by molecular packing in the crystal.

A final feature of both structures is the external angle at C(7), *i.e.* C(10)–C(7)–P. We do not find the normal

tetrahedral angle of 109.5° , but $115.4 (2)^\circ$ in D1CL and $116.5 (8)^\circ$ in D1BR. A similar angle has been found in 2,5-dimethyl-7,7-dicyanonorcaradiene (115.2°). Several authors have suggested that mutual steric or dipole–dipole repulsion causes this widening; as a consequence, the internal angle at C(7) should diminish and the C(1)–C(6) distance should be shortened, *i.e.* the norcaradiene form should be stabilized. This is not necessarily true, because similar angles have been found in cyclopropanes where no repulsion of geminal substituents should take place [*e.g.* NC–C–H in 1,2,3-tricyanocyclopropane is $116.2 \pm 1.1^\circ$ (Hartman & Hirshfeld, 1966), and H–C–H in cyclopropane-1,1-dicarboxylic acid is $119.5 \pm 5.5^\circ$ (Meester, Schenk & MacGillavry, 1971)].

The molecular arrangement in the unit cells is shown in Figs. 7 and 8. Although the crystal system is different for the two compounds, the molecular packing is very similar. Two molecules, related by a centre of symmetry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ are arranged so as to give an intermolecular halogen distance of 3.67 Å for D1CL and 3.99 Å for D1BR. This is about twice the van der Waals radius of the halogen atoms. Apparently, the packing is dominated by the halogen atoms. Some other intermolecular distances are listed in Tables 9 and 10. The shortest contacts (3.4–3.7 Å) arise from those parts of the molecules whose phosphonate groups lie towards the relating inversion centre. As expected, the molecules of D1BR are not as closely packed as in D1CL, most of the contacts being 0.2–0.3 Å longer than in D1CL.

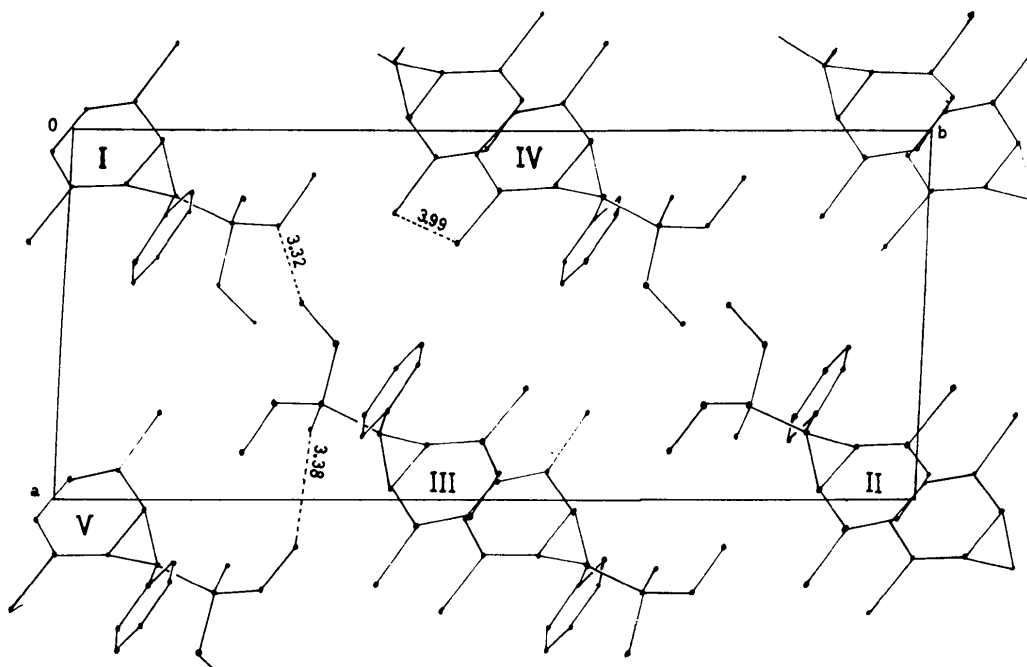


Fig. 8. Unit cell of D1BR as viewed down the c axis. Symmetry code is as in Table 9.

Table 9. Shortest intermolecular contacts in DICL (Å)

i	(\bar{x} , \bar{y} , \bar{z})	ii	(x , $1+y$, z)
iii	($1+x$, y , z)	iv	(x , y , $1+z$)
v	($1+x$, $1+y$, z)	vi	($1-x$, $1-y$, $1-z$)
vii	($1-x$, \bar{y} , \bar{z})		

O(2)—O(2 ⁱ)	3.439	O(3)—C(13 ^{iv})	3.560
O(2)—C(9 ⁱ)	3.387	O(3)—C(14 ^{iv})	3.278
C(9)—C(13 ⁱ)	3.644	Cl(1)—Cl(2 ^{vi})	3.669
C(9)—C(14 ⁱ)	3.733	Cl(1)—C(5 ^{vi})	3.595
Cl(1)—O(3 ⁱⁱ)	3.429	Cl(1)—C(6 ^{vi})	3.641
Cl(1)—C(9 ⁱⁱ)	3.685	C(1)—C(2 ^{vi})	3.702
C(11)—C(9 ⁱⁱ)	3.699	C(1)—C(3 ^{vi})	3.761
C(12)—C(9 ⁱⁱ)	3.797	C(2)—C(6 ^{vi})	3.703

Table 10. Shortest intermolecular contacts in DIBR (Å)

i	(\bar{x} , \bar{y} , \bar{z})	ii	(\bar{x} , $\frac{1}{2}-y$, $\frac{1}{2}+z$)
iii	($1-x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$)		

Br(1)—Br(2 ⁱ)	3.99	C(12)—C(9 ⁱⁱ)	3.75
Br(2)—C(5 ⁱ)	3.76	Br(1)—O(3 ⁱⁱ)	3.94
Br(2)—C(6 ⁱ)	3.85	O(2)—O(8 ⁱⁱⁱ)	3.32
C(1)—C(2 ⁱ)	3.87	C(9)—C(8 ⁱⁱⁱ)	3.98
C(1)—C(3 ⁱ)	3.86	C(11)—C(8 ⁱⁱⁱ)	3.83
C(2)—C(6 ⁱ)	3.96	C(12)—C(8 ⁱⁱⁱ)	3.69
C(9)—O(3 ⁱⁱ)	3.38	C(13)—C(8 ⁱⁱⁱ)	3.81
C(11)—C(9 ⁱⁱ)	3.88		

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