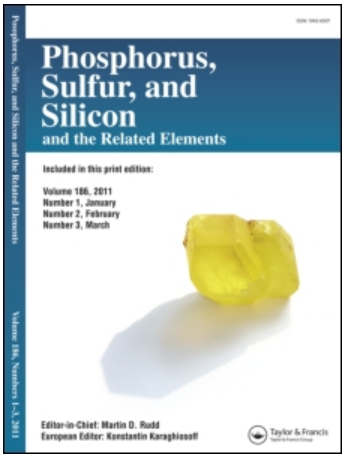

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A STRUCTURAL STUDY OF DIMETHYL 2,2-DICHLORO-1-PHENYL-1-CYCLOPROPANEPHOSPHONATE

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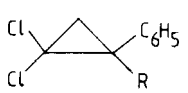
The molecular geometry of the title compound (**1**) is determined by an X-ray structure analysis. Comparison with the already known structure of 1,1-dichloro-2,2-diphenylcyclopropane (**2**) reveals the shortening influence of the P=O group on the distal cyclopropane bond, which is expected from the conjugative interaction of a π-acceptor substituent with the three-membered ring. In the ^{1}H NMR spectrum, **1** displays remarkably large ^{3}J(P,H) *cis* and *trans* coupling constants.

Structural studies of substituted cyclopropanes have met growing attention in recent years. Currently, the Cambridge Crystallographic Database contains structural data of more than 300 cyclopropanes. Many of these studies were undertaken in order to elucidate the influence of substituents on the bond geometry of the three-membered ring. Several theoretical models, partly based on simple qualitative MO considerations[1–3] and partly derived from detailed calculations,[4–6] offer predictions of the effect of π-acceptor and π-donor substituents as well as halogen atoms, which are σ-acceptors and π-donors at the same time. In a recently published paper, the experimental structural data have been checked for systematic influences of substituents, and the theoretical models could be confirmed by and large.[7]

A π-acceptor substituent is expected to lengthen the adjacent ring bonds and to shorten the opposite one, as compared to unsubstituted cyclopropane.[1] Like the carbonyl function, the P=O group is considered to act as a π-acceptor by conjugative interaction with a cyclopropane ring. Earlier, we had taken this feature to explain the stabilization of the bicyclic valence tautomer in the norcaradiene ⇌ cycloheptatriene equilibrium by a phosphonate or diphenylphosphoryl group at C-7.[8] X-ray structural studies of several compounds with a cyclopropanephosphonate moiety[9–12] qualitatively displayed the expected influence of the π-acceptor substituent; however, the overall pattern of substitution (all cyclopropane rings were part of bicyclic or tricyclic molecules) never allowed us to establish quantitatively the influence of the P=O function on the cyclopropane geometry.

Therefore, we turned to a "monocyclic" cyclopropanephosphonate. Even though highly substituted, the title compound **1** was chosen as it is structurally similar to the already investigated cyclopropane **2**.[13]



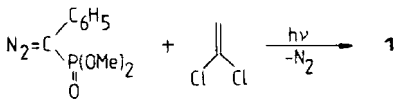
1 R = $P(O)(OMe)_2$

2 R = C_6H_5

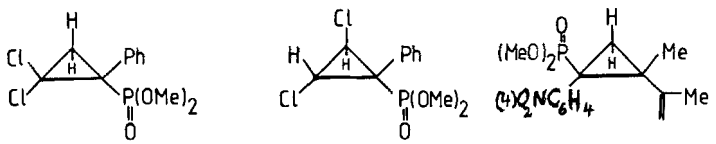
RESULTS AND DISCUSSION

Synthesis and ^{1}*H-NMR of* **1**

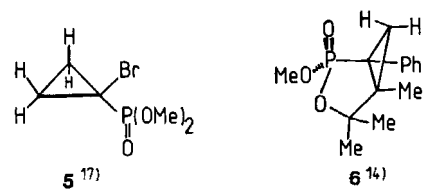
Title compound **1** was obtained in 67% yield by photolysis ($\lambda > 280$ nm) of dimethyl (diazobenzyl)phosphonate in excess 1,1-dichloroethylene.



The ^{1}H-NMR spectrum of **1** deserves some attention. The cyclopropane protons appear at $\delta = 2.11$ and 2.59 ppm as AB part of a ABX system, where X corresponds to the P nucleus. The signal at higher field comes from the proton which lies in the shielding region of the phenyl ring, i.e. on the same side of the ring plane. The ^{3}J(P,H*cis*) and ^{3}J(P,H*trans*) values are the largest P,H coupling constants found so far in "monocyclic" cyclopropanes. In our experience, a value of 12–13 Hz for the ^{3}J(P,H*trans*) coupling is usually found only in bicyclic [3.1.0] systems like **6**.[14] Taking into account the values for **1** and the closely related cyclopropane **3**,[15] one must state that the often encountered value of 12–13 Hz for a ^{3}J(P,H) coupling in a cyclopropane may indicate either a *cis* or a *trans* relation of the coupling nuclei. To be sure, one needs the values of both stereoisomers, as the relation ^{3}J(P,H*cis*) > ^{3}J(P,H*trans*) has never failed so far. Examples **3–6** illustrate the variability of P,H coupling constants in cyclopropanes (Scheme 1).



	1	**3**[15]	**4**[16]
^{3}J(P,Hcis)	18.7	15.6	18.0
^{3}J(P,Htrans)	12.8	11.2	9.9



	5[17]	**6**[14]
^{3}J(P,Hcis)	12.70	15.0
^{3}J(P,Htrans)	7.12	13.4

SCHEME 1 Coupling constants (Hz) in some selected P=O-substituted cyclopropanes.

Structural considerations for **1**

The structure of **1** is represented in Figure 1. Bond lengths and bond angles are listed in Table 3.

The overall structure. Because of steric constraints, the phenyl ring assumes a nearly perpendicular conformation relative to the three-membered ring, and the phosphoryl group is in a nearly bisecting conformation. A complete bisecting conformation would allow an ideal overlap of the substituent's π-orbitals with the in-plane Walsh orbitals of the cyclopropane, whereas for a perpendicular arrangement, there is no π-overlap at all. As a measure for the amount of overlap, one may take the angle θ between the C2–C3 vector and the normal to the plane of the phenyl ring or to the C1—P—O1 plane, resp. This angle amounts to 75.2° for the phenyl ring and to 19.4° for the C1—P—O1 plane (see Table 4); the values for true perpendicular and bisecting conformations would be 90 and 0°; resp.

The P=O group points to the cyclopropane side of the molecule, as has been found in all other similarly substituted cyclopropanes before.[8-11] With a P—Cl2 distance of 3.289 Å (sum of van der Waals radii:[18] 3.55 Å), there seems to be some repulsion between both atoms, as the Cl2—C2 distance is slightly longer than Cl1—C2, and Cl2 is also bent away from the ring somewhat more than Cl1.

Cyclopropane geometry. The three-membered ring in **1** is unsymmetrical with one short and two long C—C bonds. In fact, the geometry is very similar to the one

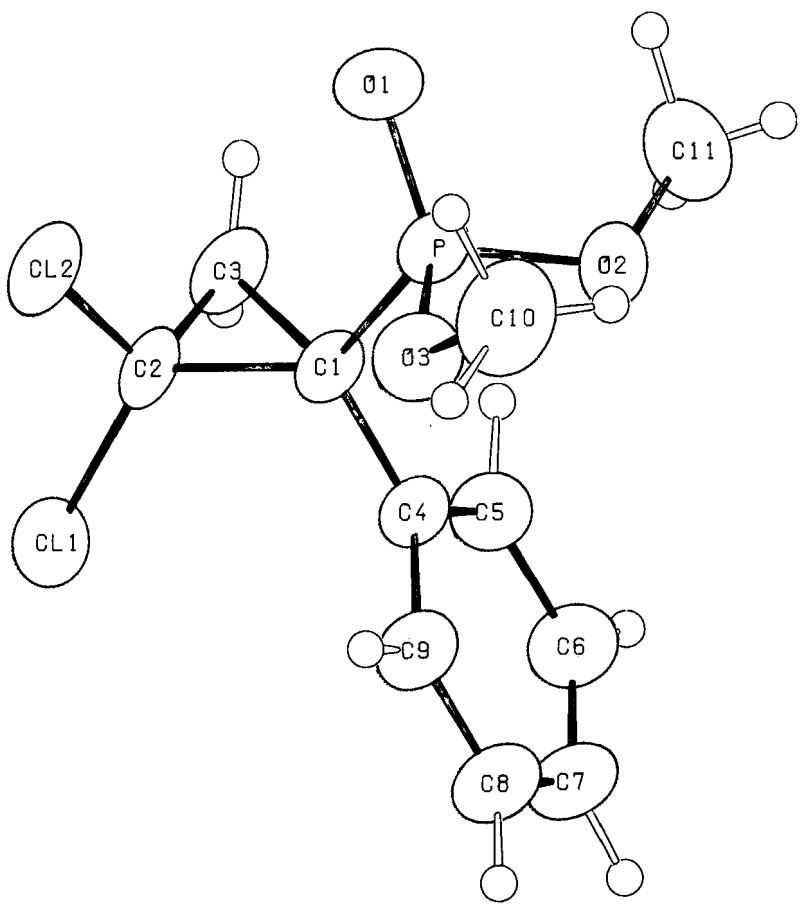


FIGURE 1 ORTEP[24] plot of 1. The ellipsoids are drawn on the 50% probability level.

TABLE 1

Atomic coordinates and thermal parameters ($*10^4$) of **1**. Esd's are in parentheses. The temperature factor expression has the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl1	2628(1)	642(2)	9653(1)	111(1)	161(2)	46(1)	35(3)	49(2)	−14(2)
Cl2	2977(1)	−2203(1)	8888(1)	118(1)	101(1)	72(1)	33(2)	69(2)	58(2)
P	2741(1)	−761(1)	6636(1)	60(1)	84(1)	46(1)	8(2)	40(1)	−4(2)
O1	3621(3)	−1985(3)	6791(2)	88(3)	86(4)	79(2)	34(6)	75(5)	−4(5)
O2	2718(3)	319(4)	5735(2)	103(3)	134(5)	59(2)	36(7)	84(5)	23(5)
O3	1318(3)	−1144(4)	6344(2)	68(3)	142(5)	57(2)	−22(6)	35(4)	−46(5)
C1	3021(3)	408(4)	7759(3)	48(3)	84(5)	46(2)	1(7)	25(5)	8(6)
C2	3185(4)	−296(5)	8796(3)	73(4)	100(6)	44(3)	12(8)	25(5)	7(6)
C3	4311(4)	235(5)	8617(3)	54(4)	113(6)	61(3)	14(8)	4(5)	6(7)
C4	2450(4)	1918(4)	7533(3)	55(3)	84(5)	41(2)	4(7)	27(5)	−1(6)
C5	3189(4)	3116(5)	7515(3)	67(4)	97(6)	64(3)	−14(8)	58(6)	−23(7)
C6	2670(5)	4507(5)	7298(4)	118(5)	72(5)	85(4)	−20(9)	100(8)	−3(8)
C7	1409(5)	4708(5)	7110(4)	117(6)	89(6)	85(4)	76(10)	79(8)	14(8)
C8	672(4)	3528(6)	7130(4)	73(5)	130(7)	87(4)	28(9)	57(7)	5(9)
C9	1180(4)	2124(5)	7329(4)	65(4)	94(6)	67(3)	1(8)	38(6)	13(7)
C10	634(5)	−1895(6)	5378(4)	111(6)	158(8)	68(4)	−67(11)	19(7)	−58(9)
C11	3841(6)	606(7)	5530(5)	187(9)	158(9)	133(6)	30(15)	227(13)	60(12)

TABLE 2

Positional parameters ($*10^3$) and isotropic temperature factor for hydrogen atoms. Esd's are in parentheses

Atom	x/a	y/b	z/c	B[Å^2]
H3.1	482(4)	−47(5)	850(3)	1.2(0.9)
H3.2	474(4)	109(5)	894(3)	1.7(1.0)
H5	407(3)	296(4)	766(3)	0.0(0.7)
H6	316(4)	529(6)	729(4)	2.7(1.1)
H7	108(4)	567(5)	701(3)	1.5(0.9)
H8	−12(5)	360(6)	704(4)	3.9(1.3)
H9	70(4)	132(5)	737(3)	2.0(1.0)
H10.1	−12(5)	−217(6)	545(4)	3.1(1.2)
H10.2	99(7)	−285(8)	540(5)	7.6(2.0)
H10.3	70(6)	−132(7)	483(5)	6.0(1.7)
H11.1	367(6)	102(7)	497(5)	6.5(1.8)
H11.2	427(6)	128(7)	598(5)	6.0(1.6)
H11.3	429(5)	−30(7)	555(4)	4.9(1.4)

found in **2**,[13] as can be seen in Figure 2. C1–C2 and C1–C3 distances are equal in both structures, only C2–C3 is significantly shorter in **1** than in **2** (1.490(3) Å).

The bond length asymmetry roughly corresponds to the expectations for the substituent effects: A chlorine substituent on a cyclopropane causes shortening of the vicinal bonds and lengthening of the distal bond.[7] An example is the geometry of 1,1-dichlorocyclopropane,[19] where C1–C2 = 1.480 Å and C2–C3 = 1.544 Å. According to a recent theoretical study,[6] neither the σ-electron acceptor nor the π-donating capabilities of chlorine, but "local effects such as changes in hybridization and steric interaction" play the major role in these geometrical changes. A π-acceptor substituent, on the other hand, which in a bisecting conformation can efficiently interact with a filled cyclopropane molecular orbital of appropriate symmetry, lengthens the adjacent cyclopropane bonds and shortens the distal one.

If one accepts the P=O group as a π-acceptor substituent in **1**, the combination of the effects of chlorine substitution at C2 and P=O substitution at C1 yields qualitatively the bond length distributions found experimentally, with C2–C3 as shortest and C1—C3 as longest bond. However, as *Ibers et al.* have pointed out,[20,21] the

TABLE 3

Bond lengths (Å) and bond angles (degrees)

Cl1—C2	1.746(4)	Cl2—C2	1.760(5)	P—O1	1.461(3)
P—O2	1.574(3)	P—O3	1.564(3)	P—C1	1.809(4)
O2—C11	1.428(7)	O3—C10	1.452(6)	C1—C2	1.516(6)
C1—C3	1.534(5)	C1—C4	1.503(6)	C2—C3	1.470(6)
C4—C5	1.382(6)	C4—C9	1.386(6)	C5—C6	1.382(6)
C6—C7	1.379(7)	C7—C8	1.368(7)	C8—C9	1.387(7)
Cl2—C2—Cl1	110.0(2)	C1—C2—Cl1	118.6(3)	C3—C2—Cl1	120.0(3)
C1—C2—Cl2	120.6(3)	C3—C2—C12	118.9(3)	O2—P—O1	114.2(2)
O3--P—O1	117.6(2)	C1—P—O1	114.7(2)	O3—P—O2	102.1(2)
C1—P—O2	104.8(2)	C11—O2—P	120.2(3)	C1—P—O3	101.8(2)
C10—O3—P	120.7(3)	C2—C1—P	118.9(3)	C3—C1—P	115.5(3)
C4—C1—P	115.3(3)	C3—C1—C2	57.6(3)	C4—C1—C2	118.7(3)
C4—C1—C3	118.6(3)	C3—C2—C1	61.8(3)	C2—C3—C1	60.6(3)
C5—C4—C1	120.1(3)	C9—C4—C1	120.6(4)	C9—C4—C5	119.2(4)
C6—C5—C4	120.6(4)	C8—C9—C4	119.8(4)	C7—C6—C5	119.9(4)
C8—C7—C6	119.9(4)	C9—C8—C7	120.6(4)		

TABLE 4

Interplanar and Vector-Plane[a] Angles θ (degrees)

C1—C2—C3 and P1—C1—C4	88.1
C4—C5—C6—C7—C8—C9	57.9
C1—P—O1	77.8
P—C1—C4 and C1—P—O1	20.3
C2—C3 and P—C1—C4	3.0
C4—C5—C6—C7—C8—C9	75.2
C1—P—O1	19.4

[a] A vector-plane angle is the acute angle between the vector and the normal of the plane.

observed bond length differences in highly substituted cyclopropanes cannot be split into independent contributions of the individual substituents.

Therefore, if one wants to know the magnitude of the bond length assymmetry induced by a P=O substituent, one can only estimate which change takes place on replacing one phenyl group in **2** by $PO(OMe)_2$ to give **1**. As stated above, the adjacent bonds C1–C2 and C1–C3 remain unaffected within the error limits, and only the distal bond C2–C3 becomes significantly shorter by 0.02 Å. As the P=O-group is close to a bisecting conformation relative to the cyclopropane ring (see above), it can act as a π-acceptor, i.e. shorten the distal bond as observed, but also lengthen the vicinal bonds which is not found. Of course, one must also consider the consequences of removing a phenyl group from **2**. Both phenyl rings in **2** assume nearly perpendicular conformations relative to the three-membered ring[13] (θ = 78.6 and 74.1°), comparable to the phenyl ring in **1**; therefore, they cannot induce a cyclopropane bond length asymmetry by the π-acceptor mechanism. It has been suggested, however, that phenyl rings in the perpendicular conformation act as π-donors to an unfilled cyclopropane molecular orbital, which would result in a shortened distal bond.[21] If this assumption is true, the net effect of the phosphoryl group in **1** would be a shortening of the distal bond by *more* than 0.02 Å.

Ab initio calculations for cyclopropane have shown[22] that by increasing an exocyclic HCH angle, the adjacent ring bonds will become longer and the distal bond will be shortened. This effect, if at all, should be of minor importance when going from **2** to **1**, as the exocyclic angle at C1 is increased by only 1.4° (see Figure 2).

In summary, one may conclude, that the P=O group has a distinct effect at least on the opposite cyclopropane bond length, if it is in the right conformation to act as a π-acceptor. The estimate given by *Allen*[7] for the shortening of this bond (ca. 0.01 Å) probably represents the lower limit of the change to be expected.

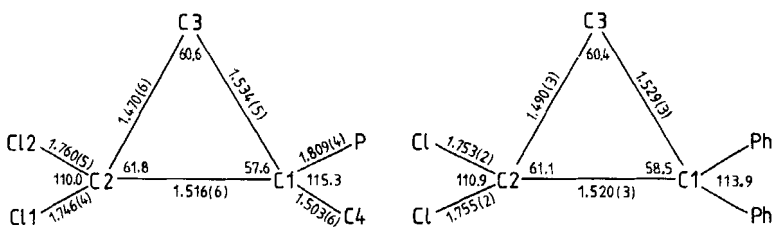


FIGURE 2 Cyclopropane geometries of **1** (left) and **2**[13] (right). The numbering in **2** was chosen as to allow an easier comparison with **1** (see text).

EXPERIMENTAL

Preparation of 1. 4.00 g (17.7 mmol) dimethyl(diazobenyl)phosphonate[23] in 50 ml 1,1-dichloroethylene are irradiated for 6 hours (Philips HPK 125 W, high-pressure mercury lamp). Efficient cooling of the solution is necessary. The lamp-side wall of the photolysis vessel becomes gradually covered by a polymer, and must be cleaned once or twice during irradiation time. At the end, the solution is filtered, and the solvent is evaporated. Upon addition of 10 ml ether, 3.50 g (67%) colorless crystals of *dimethyl 2,2-dichloro-1-phenyl-1-cyclopropanephosphonate* are obtained, m.p. 94°C. Anal. Calc. for $C_{11}H_{13}Cl_2O_3P$ (295.10): C, 44.77; H, 4.44. Found: C, 44.82; H, 4.49.-IR(KBr): 1262 (P=O); 1080, 1060, 1034, 1026 cm^{-1} (P—O—C region).-^{1}H-NMR($CDCl_3$, δ): 2.11 and 2.59 (AB part of ABX system, where X=P, J_{AX} = 12.8 Hz, J_{BX} = 18.7 Hz, $|J_{AB}|$ = 6.6 Hz), 3.57 and 3.60 (two d, J = 10.8 Hz each, diastereotopic $POCH_3$), 6.85–7.95 (broad, 5H-Phenyl).

X-Ray Analysis of 1. *Crystal data.* a = 11.386(5), b = 9.089(3), c = 13.769(5) Å, β = 110.70(4)°; V = 1333(3) Å^3; Z = 4; D_{calc} = 1.470 g cm^{-3}; Space group P $2_1/c$; μ(MoKα) = 5.99 cm^{-1}.

Data collection and structure solution: A crystal with maximum size 0.25·0.18·0.13 mm^3 was used for data collection on a Philips PW 1100 four-circle diffractometer. Exact lattice constants were obtained from diffractometer settings of 25 reflections. With Zr-filtered MoKα radiation, 2477 unique reflections were measured in the range $1.50 < \theta < 25.50°$ ($\theta/2\theta$-scan, scan speed 0.03°/sec, scan width (1.10 + 0.35 tanθ)). Three reference reflections were monitored every hour; the observed intensity loss of 3.4% was corrected linearly. Lorentz and polarization, but no absorption corrections were applied. The structure was solved with MULTAN 77 and refined by block-diagonal least-squares methods.[24] Hydrogen atoms were located in a ΔF synthesis and included in the refinement procedure with isotropic B's. The weighting scheme of the last cycles was $w = 1$ for $F_0 < 40.7$, otherwise $w = 40.7/F_0$. The strongest reflection (200) was excluded at the end. With 1662 reflections having $F_0 > 4\sigma(F_0)$, refinement converged at R = 4.45%, $R_w = \Sigma w\Delta^2 F/\Sigma w F_0^2$ = 5.41%. Atomic coordinates and thermal parameters are listed in Tables 1 and 2.

ACKNOWLEDGMENT

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