

## THE CRYSTAL STRUCTURE OF 1,1-DIMETHYL-2,3,4,5-TETRAPHENYL-1-SILACYCLOPENTADIENE

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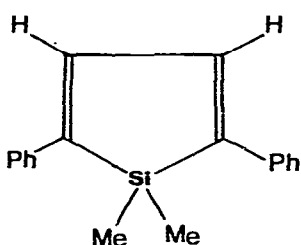
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### Summary

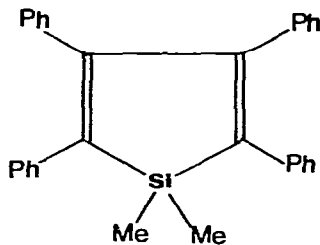
1,1-Dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene crystallizes in the  $P2_1/c$  space group,  $Z = 8$ . The two molecules in the asymmetric unit mainly differ in the rotations of the phenyl groups with respect to the silacyclopentadiene ring, presumably as a result of crystal packing forces. The geometry of the silole ring in the title compound deviates considerably from that observed in 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene. Mean bond distances and angles in the silole ring are Si—C 1.868(3), C=C 1.358(2), C—C 1.511(2) Å, C—Si—C 92.7(1), Si—C=C 107.6(2), C=C—C 116.0(1)°.

### Introduction

Since the first report [1] on silacyclopentadienes, such compounds have attracted attention because of their unusual colour reactions. 1-Alkyl or -aryl derivatives (containing an activated hydrogen atom attached to silicon) react with *n*-butyl or phenyllithium to yield black-violet solids [2]. These products are *n*-butyl (phenyl) derivatives, the silacyclopentadiene ring is substituted by lithium to form a C—Li covalent bond [3]. 1,1-Dialkyl or -diaryl derivatives react with alkali metals giving radical anions or di-anions in solution with colours ranging from blue to violet [4].



[I]



[II]

Several examples of silole complexes have been reported [e.g. 5, 6 and references therein]. The crystal structure of uncomplexed, 1,1-dimethyl-1,2-diphenyl-1-silacyclopentadiene [I] has been previously studied [6] to give structural information upon the silole ring. Crystal structure determinations of diphenylacetylene · I [5] and tricarbonylruthenium · I complexes [6] have also been published but without detailed molecular geometries.

## Experimental

The crystals of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene [II] were kindly supplied by Professor Rühlmann [2].

Intensity data were collected on a computer-controlled Enraf-Nonius CAD-4 diffractometer with Cu- $K_{\alpha}$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at room temperature. Unit cell parameters were determined and refined using the setting angles of 25 carefully centered reflections. Crystal data and data collection parameters are given in Table 1.

### *Solution and refinement of the structure*

The structure was solved by direct methods (MULTAN program [7] (Enraf-Nonius SDP program package),  $429 E \geq 2.1$ ) and Fourier techniques. After solution of the structure all reflections with zero intensity were eliminated from the data set.

3972 reflections [ $F_0 \geq 5\sigma(F_0)$ ] were used in the full-matrix isotropic refinement ( $R = 0.11$ ). At this stage all hydrogen atoms were generated from assumed geometries (methyl hydrogen atomic positions were calculated accomplishing staggered conformation). 6487 reflections [ $F_0 \geq 1\sigma(F_0)$ ] were used in a full-matrix anisotropic least-squares refinement. To reduce computing time the two molecules were refined separately, but in two final cycles both molecules were simultaneously refined. The weighting scheme applied was:

$$w = 4 F_0^2 L_p^2 / [\sigma(I)^2 + (0.01 I)^2]$$

where  $F_0$  is the structure factor,  $I$  is the observed intensity and  $L_p$  is the Lorenz-polarization factor.

TABLE 1  
CRYSTAL DATA AND DATA COLLECTION PARAMETERS

Empirical formula: $C_{30}H_{26}Si$	Formula weight: 414.6
Cell constants: $a$ 9.103(1), $b$ 18.674(2), $c$ 30.603(4) $\text{\AA}$ , $\beta$ 113.22(2) $^\circ$ , $V$ 4780.8(2.0) $\text{\AA}^3$	
Space group $P2_1/c$ , $Z = 8$	
Calculated density ( $\text{mg/m}^3$ )	1.152
$\mu$ (Cu- $K_{\alpha}$ ) (mm)	9.371
Approx. crystal size (mm)	$0.18 \times 0.20 \times 0.25$
$2\theta$ range ( $^\circ$ )	$3 < 2\theta < 150$
Scan width ( $^\circ$ )	$0.35 + 0.35 \ln \theta$
Max. scan time (min)	0.5
Scan technique	$\theta-2\theta$
Number of reflections collected:	10120
Number of reflections with zero intensity:	3585

TABLE 2

ATOMIC COORDINATES OF THE NON-HYDROGEN ATOMS AND  $B(\text{eq})$  VALUES <sup>a</sup>

Atom	Molecule A				Molecule B			
	$10^4 x$	$10^4 y$	$10^5 z$	$B(\text{eq})$	$10^4 x$	$10^4 y$	$10^5 z$	$B(\text{eq})$
Si	3751(1)	4100(03)	37403(2)	4.88(3)	7414(1)	1469(03)	35058(2)	4.19(2)
C(1)	4664(2)	4800(1)	34914(7)	4.2(1)	6877(2)	758(1)	38456(7)	3.8(1)
C(2)	4330(2)	5446(1)	36302(7)	3.8(1)	7717(2)	159(1)	38358(6)	3.6(1)
C(3)	3467(2)	5434(1)	39634(7)	3.9(1)	8652(2)	197(1)	35243(7)	3.7(1)
C(4)	3031(2)	4775(1)	40596(7)	4.3(1)	8636(2)	835(1)	33105(7)	3.9(1)
C(5)	5138(4)	3443(2)	41538(9)	7.7(2)	8638(3)	2160(1)	39332(9)	5.9(1)
C(6)	2162(4)	3624(2)	32464(10)	7.9(1)	5734(3)	1902(1)	30194(8)	5.9(1)
C(7)	5406(2)	4661(1)	31472(7)	4.4(1)	5883(2)	858(1)	41212(7)	4.2(1)
C(8)	6502(3)	4112(1)	32307(9)	7.2(1)	4368(3)	1154(1)	39066(8)	6.3(1)
C(9)	7184(3)	3945(2)	29108(9)	8.1(1)	3417(3)	1275(2)	41591(9)	8.1(1)
C(10)	6754(3)	4313(1)	24941(8)	6.4(1)	3984(3)	1115(2)	46313(8)	8.2(1)
C(11)	5651(3)	4854(1)	23991(7)	5.7(1)	5482(3)	828(2)	48554(8)	6.9(1)
C(12)	4986(3)	5028(1)	27204(7)	4.9(1)	6416(3)	626(1)	46018(7)	5.3(1)
C(13)	4777(2)	6143(1)	34834(6)	3.8(1)	7772(2)	-515(1)	41012(6)	3.8(1)
C(14)	6365(3)	6298(1)	35729(8)	4.7(1)	9184(3)	-731(1)	44615(8)	5.3(1)
C(15)	6769(3)	6955(1)	34346(8)	5.6(1)	9262(3)	-1368(1)	47001(8)	6.5(1)
C(16)	5614(3)	7448(1)	32024(8)	5.6(1)	7945(3)	-1801(1)	45778(7)	6.0(1)
C(17)	4040(3)	7300(1)	31078(8)	5.0(1)	6536(3)	-1588(1)	42228(8)	5.7(1)
C(18)	3618(2)	6654(1)	32497(7)	4.4(1)	6454(3)	-950(1)	39860(7)	4.7(1)
C(19)	3152(2)	6116(1)	41654(7)	3.8(1)	9487(2)	-462(1)	34756(7)	4.3(1)
C(20)	4407(2)	6562(1)	44356(7)	4.4(1)	8601(3)	-1042(1)	32255(8)	5.6(1)
C(21)	4112(3)	7176(1)	46389(7)	5.0(1)	9339(3)	-1667(1)	31857(9)	8.0(2)
C(22)	2591(3)	7360(1)	45782(8)	5.9(1)	10951(3)	-1721(1)	33969(10)	10.1(2)
C(23)	1333(3)	6925(1)	43095(8)	6.0(1)	11870(3)	-1154(2)	36409(10)	9.4(1)
C(24)	1612(3)	6303(1)	41021(8)	4.3(1)	11121(3)	-508(1)	36769(9)	6.4(1)
C(25)	2340(2)	4602(1)	44107(7)	4.1(1)	9393(2)	982(1)	29740(7)	4.0(1)
C(26)	2832(2)	4933(1)	48537(7)	4.7(1)	9483(2)	480(1)	26472(7)	5.1(1)
C(27)	2212(3)	4728(1)	51789(8)	5.4(1)	10225(3)	638(1)	23427(8)	6.4(1)
C(28)	1103(3)	4191(1)	50793(8)	6.3(1)	10900(3)	1302(2)	23570(8)	6.5(1)
C(29)	630(3)	3842(2)	46499(9)	7.7(1)	10800(3)	1801(1)	26642(9)	7.0(1)
C(30)	1241(3)	4048(1)	43180(9)	7.1(1)	10049(3)	1650(1)	29672(8)	5.5(1)

<sup>a</sup> Defined as follows:  $4[(b_{11}b_{22}b_{33})/(a^2b^2c^2)]^{1/3}$  (Å<sup>2</sup>)

At the end of the refinement hydrogen coordinates were re-calculated [ $C(sp^3)-H = 1.086$ ,  $C(sp^2)-H = 1.040$  Å]. The final  $R$  values are  $R_0 = 0.063$ ,  $R_w = 0.056$ ,  $R_{tot} = 0.064$ . Atomic scattering factors and anomalous dispersion coefficients were taken from ref. 8. The final atomic parameters are given in Tables 2 and 3. All calculations were performed on a PDP 11/34 (64K) mini-computer using the E.N. SDP program package and local programs.

### Description of the structure

The two molecules of the asymmetric unit are depicted in Fig. 1 (atoms of molecule B are denoted with stars). Relevant bond lengths and angles are given in Table 4. The averaged geometry of the core of the molecule is shown in Fig. 2. The silole ring geometry is considerable different from that observed in I. The central C—C (single) bond lengths in the conjugated diene system betray reduced delocalization of the double bonds (mean C—C (single) 1.511(2) Å vs.

TABLE 3  
CALCULATED HYDROGEN ATOMIC COORDINATES <sup>a</sup>

Atom	Molecule A			Molecule B		
	10 <sup>3</sup> x	10 <sup>3</sup> y	10 <sup>4</sup> z	10 <sup>3</sup> x	10 <sup>3</sup> y	10 <sup>4</sup> z
H(5A)	446	307	4273	897	258	3741
H(5B)	577	315	3972	795	239	4119
H(5C)	600	372	4459	972	192	4189
H(6A)	271	325	3085	511	226	3169
H(6B)	140	334	3384	619	221	2799
H(6C)	146	401	2981	492	149	2804
H(8)	683	382	3543	393	129	3548
H(9)	803	354	2989	228	149	3989
H(10)	725	419	2252	328	121	4822
H(11)	531	514	2082	592	71	5217
H(12)	416	544	2641	754	46	4774
H(14)	725	592	3743	1020	-41	4554
H(15)	796	707	3509	1033	-152	4974
H(16)	593	794	3098	801	-229	4752
H(17)	316	767	2929	553	-191	4132
H(18)	243	655	3181	538	-80	3717
H(20)	557	643	4484	736	-100	3066
H(21)	506	750	4841	866	-210	2994
H(22)	238	782	4733	1150	-220	3374
H(23)	17	706	4261	1311	-120	3798
H(24)	66	598	3899	1180	-7	3855
H(26)	368	534	4940	898	-2	2633
H(27)	259	499	5506	1027	26	2102
H(28)	63	405	5325	1148	142	2133
H(29)	-19	342	4573	1130	231	2672
H(30)	87	378	3994	997	205	3196

<sup>a</sup> *B* values of the hydrogen atoms are calculated from the *B*(eq) values of the carbon atoms to which they are bonded [*B*(H) = *B*(eq) + 1 (Å<sup>2</sup>)].

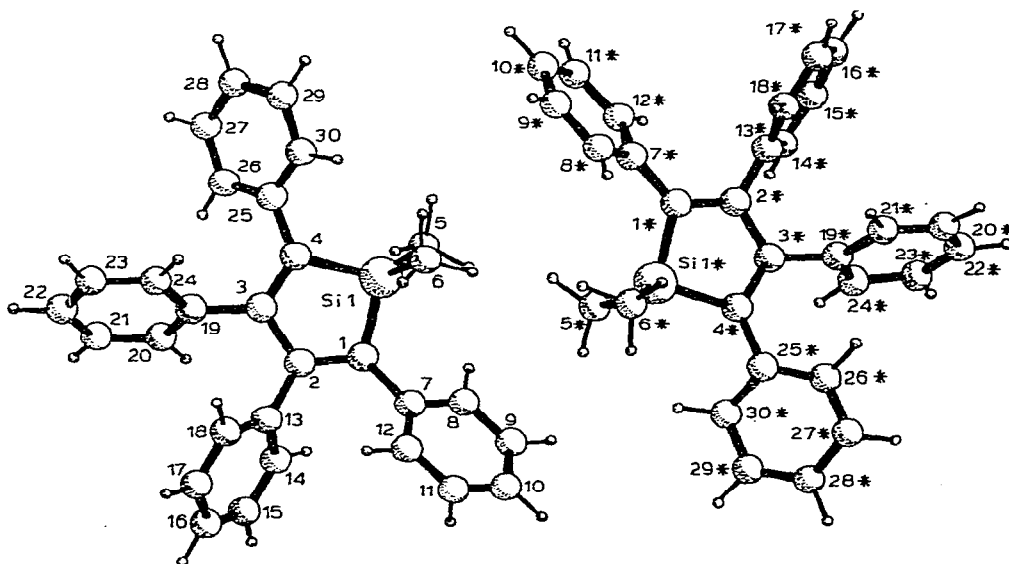


Fig. 1. A view of the asymmetric unit with the numbering of the atoms (isolated numbers denote carbon atoms).

TABLE 4

RELEVANT BOND DISTANCES (Å) AND ANGLES (°) WITH THEIR E.S.D.'s<sup>a</sup>

Si—C(1)	1.865(2)	C(1)—C(2)	1.354(3)	C(3)—C(4)	1.359(3)
	1.867(2)		1.361(3)		1.357(3)
Si—C(4)	1.865(2)	C(1)—C(7)	1.481(2)	C(3)—C(19)	1.492(3)
	1.876(2)		1.472(2)		1.484(3)
Si—C(5)	1.854(3)	C(2)—C(3)	1.513(2)	C(4)—C(25)	1.480(2)
	1.863(2)		1.509(2)		1.473(2)
Si—C(6)	1.855(3)	C(2)—C(13)	1.485(3)		
	1.848(2)		1.488(3)		
Mean C—C in phenyl-groups:			1.382(2)		
			1.379(2)		
C(1)—Si—C(4)	92.6(1)	C(1)—C(2)—C(13)	124.4(3)		
	92.7(1)		125.5(3)		
C(1)—Si—C(5)	116.7(2)	C(3)—C(2)—C(13)	119.6(3)		
	108.5(2)		118.6(3)		
C(1)—Si—C(6)	109.4(2)	C(2)—C(3)—C(4)	115.7(3)		
	116.4(2)		116.3(3)		
C(4)—Si—C(5)	112.0(2)	C(2)—C(3)—C(19)	120.1(3)		
	113.3(2)		117.6(3)		
C(4)—Si—C(6)	115.4(2)	C(4)—C(3)—C(19)	124.2(3)		
	115.2(2)		126.0(3)		
C(5)—Si—C(6)	110.0(2)	Si—C(4)—C(3)	107.8(2)		
	109.7(2)		107.2(2)		
Si—C(1)—C(2)	107.8(2)	Si—C(4)—C(25)	124.8(2)		
	107.4(2)		127.2(2)		
Si—C(1)—C(7)	124.7(2)	C(3)—C(4)—C(25)	126.8(3)		
	125.7(2)		125.6(3)		
C(2)—C(1)—C(7)	126.9(3)	C(8)—C(7)—C(12)	116.8(3)		
	126.5(3)		117.2(3)		
C(1)—C(2)—C(3)	116.0(3)	C(14)—C(13)—C(18)	118.4(3)		
	115.9(3)		118.4(3)		
		C(20)—C(19)—C(24)	118.8(3)		
			119.4(3)		
		C(26)—C(25)—C(30)	117.3(3)		
			116.5(3)		

<sup>a</sup> The values in the second lines refer to molecule B. (All C(sp<sup>3</sup>)-H and C(sp<sup>2</sup>)-H bond lengths are 1.086 and 1.040 Å, respectively).

1.466(6) Å reported for I). The C=C double bonds [mean 1.358(2) Å], however, are even less localized than in I [1.345(4) Å] and the ring Si—C bonds [mean 1.868(3) Å] are shorter by 0.01 Å [1.878(3) Å]. This finding is consistent with partial delocalization through the silicon atom but not through the butadiene system.

It may have C<sub>2</sub> symmetry, with the two-fold axis intersecting the C(2)—C(3) bond and passing through the silicon atom. Molecule A is fairly symmetric, equivalent bond lengths and angles being identical within experimental error. The five-membered ring is almost planar (c.f. Tables 5 and 6), the total ring puckering amplitude *Q* [9] is 0.04 Å. Rotations of the phenyl groups with respect to the silacyclopentadiene ring conform to two-fold symmetry. The dihedral angles formed by the five-membered ring and the phenyl groups in  $\alpha$ -positions to silicon are smaller [mean 44.9(2.0)°] than dihedral angles formed by the phenyl rings in  $\beta$ -position and the five-membered ring [mean 57.8(3)°].

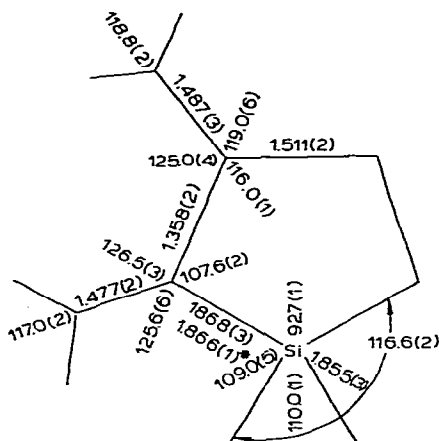


Fig. 2. Averaged bond lengths (Å) and angles ( $^{\circ}$ ) (\* Calculated without Si $^{4*}$ -C(4 $^{*}$ )).

Dihedral angles formed by the  $\beta$ -phenyl groups and the five-membered ring in molecule B are larger by ca.  $10^{\circ}$  than the corresponding values observed in molecule A. The smallest of the phenyl group—silacyclopentadiene ring dihedral angles in the whole structure is that formed by the C(25 $^{*}$ )...C(30 $^{*}$ ) phenyl

TABLE 5  
LEAST-SQUARES PLANES <sup>a</sup>

Plane	A	B	C	D	Mean deviation from plane (Å)	$\chi^2$	
1. Silacyclopentadiene ring	-0.5987 -0.5284	0.0642 -0.2772	-0.7984 -0.8025	-7.2613 -9.9708	0.015(2) 0.027(2)	621 3872	
2. C(7)...C(12)	-0.6136 -0.3264	-0.6526 -0.9178	-0.4445 -0.2260	-10.2988 -4.2135	0.004(3) 0.005(3)	23 28	
3. C(13)...C(18)	0.2576 0.5719	-0.4011 -0.4746	-0.8791 -0.6690	-13.1750 -6.0462	0.004(2) 0.003(2)	28 18	
4. C(19)...C(24)	0.2431 0.4245	0.5165 0.3358	-0.8211 -0.8409	-4.2410 -6.6113	0.001(2) 0.008(3)	5 80	
5. C(25)...C(30)	-0.6409 -0.6521	0.6620 0.3236	-0.3885 -0.6856	2.9044 -8.3646	0.007(3) 0.007(3)	60 72	
<i>Dihedral angles (<math>^{\circ}</math>)</i>							
1-2:	47.1 52.5	2-3:	60.4 66.4	3-4:	54.7 49.8	4-5:	59.7 65.9
1-3:	58.5 68.5	2-4:	83.0 74.1	3-5:	-84.9 -86.1		
1-4:	57.1 69.1	2-5:	82.3 85.9				
1-5:	42.6 36.4						

<sup>a</sup> The equation of the planes is of the form:  $AX + BY + CZ - D = 0$  where  $X, Y, Z$  are orthogonalized coordinates (The values in the second lines refer to molecule B).

TABLE 6  
RELEVANT TORSION ANGLES ( $^{\circ}$ ) WITH THEIR E.S.D.'s <sup>a</sup>

<i>In the silacyclopentadiene ring</i>			
Si—C(1)—C(2)—C(3)	4.4(2)	C(3)—C(4)—Si—C(1)	0.7(2)
	-6.6(2)		-4.0(2)
C(1)—C(2)—C(3)—C(4)	-4.2(3)	C(4)—Si—C(1)—C(2)	-2.9(2)
	3.9(3)		6.0(2)
C(2)—C(3)—C(4)—Si	1.6(2)		
	1.1(2)		
<i>Torsion angles involving atoms of the phenyl groups</i>			
Si—C(1)—C(7)—C(12)	127.2(4)	C(2)—C(3)—C(19)—C(20)	-58.6(3)
	-123.2(4)		69.7(3)
Si—C(1)—C(7)—C(8)	-48.5(3)	C(2)—C(3)—C(19)—C(24)	123.8(3)
	54.5(3)		-109.8(4)
C(2)—C(1)—C(7)—C(8)	141.1(4)	C(4)—C(3)—C(19)—C(20)	121.1(3)
	-133.7(4)		-109.6(3)
C(2)—C(1)—C(7)—C(12)	-43.1(3)	C(4)—C(3)—C(19)—C(24)	-56.6(3)
	48.7(3)		70.8(3)
C(1)—C(2)—C(13)—C(14)	-57.2(3)	C(3)—C(4)—C(25)—C(26)	-38.5(3)
	-113.7(3)[66.3]		34.7(3)
C(1)—C(2)—C(13)—C(18)	122.3(3)	C(3)—C(4)—C(25)—C(30)	146.7(4)
	68.6(3)[-111.4]		-145.9(4)
C(3)—C(2)—C(13)—C(14)	121.8(3)	Si—C(4)—C(25)—C(26)	131.3(4)
	66.6(3)[-113.4]		-142.6(4)
C(3)—C(2)—C(13)—C(18)	-58.8(3)[121.2]	Si—C(4)—C(25)—C(30)	-43.5(3)
	-111.0(3)		36.7(2)

<sup>a</sup> The values in the second lines refer to molecule B.

group and the Si<sup>\*</sup>...C(4<sup>\*</sup>) silole ring (36.4 $^{\circ}$ ). This seems to affect the Si<sup>\*</sup>—C(4<sup>\*</sup>) bond [the longest Si—C bond observed in the structure, 1.876(2) Å] rather than the C(3<sup>\*</sup>)—C(4<sup>\*</sup>) multiple bond. The distortion of the two-fold molecular symmetry in molecule B is presumably due to crystal packing forces and results in a somewhat more puckered silacyclopentadiene ring ( $Q = 0.07$  Å).

The internal angles in the phenyl rings at the bridging carbon atoms are slightly different for phenyl groups in  $\alpha$  and  $\beta$  positions [mean values: 117.1(2) $^{\circ}$  at C(7) and C(25) atoms and 118.6(2) $^{\circ}$  at C(13) and C(19) atoms] showing that C(1) (C(4)) and C(2) (C(3)) atoms are of different nature [10]. Splitting of the  $\gamma_{C_{Ar}C_{Ar}}$  IR bands also supports the non-equivalence of phenyl groups [11].

In spite of the conformational differences between molecules A and B, equivalent bond lengths and angles are in fair agreement in the silacyclopentadiene skeleton.

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### References

- 1 E.H. Braye and W. Hübel, *Chem. Ind. (London)*, (1959) 1250.
- 2 K. Rühlmann, *Z. Chem.*, 5 (1965) 354.

- 3 M.D. Curtis, *J. Amer. Chem. Soc.*, 89 (1967) 4241.
- 4 K. Rühlmann, V. Hagen and K. Schiller, *Z. Chem.*, 7 (1967) 353.
- 5 J. Clardy and T.J. Barton, *J. Chem. Soc. Chem. Commun.*, (1972) 690.
- 6 K. Muir, R. Walker, E.W. Abel, T. Blackmore and R.J. Whitley, *J. Chem. Soc. Chem. Commun.*, (1975) 698.
- 7 G. Germain, P. Main and M.M. Woolfson, *Acta Cryst. A*, 27 (1971) 368.
- 8 J.A. Ibers and W.C. Hamilton (Eds.), *International Tables for X-ray Crystallography*, Vol. 4. The Kynoch Press, Birmingham, England, 1974.
- 9 D. Cremer and J.A. Pople, *J. Amer. Chem. Soc.*, 97 (1975) 1354.
- 10 A. Domenicano, A. Vaciago and C.A. Coulson, *Acta Cryst. B*, 31 (1975) 221.
- 11 G. Pongor, J. Réffy and J. Nagy: *Periodica Polytechn. (Chem. Eng.) (Budapest)*, 18 (1974) 117.