# Crystal and Molecular Structure of an Eight-membered Cyclic Imido-sulphite, 2-(2,4,6-Trichlorophenylimino)perhydro-1,3,2,6-dioxathiazocine

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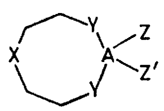
2-(2,4,6-Trichlorophenylimino)perhydro-1,3,2,6-dioxathiazocine crystallises in the triclinic space group $P\bar{1}$, with four molecules in a unit cell of dimensions $a$ = 10.725(4), $b$ = 11.730(2), $c$ = 12.451(3) Å, $\alpha$ = 108.15(8), $\beta$ = 92.92(7), $\gamma$ = 93.50(7)°. The structure was refined to $R$ 0.048 for 5 024 reflections. Two pseudo-enantiomorphic independent molecules are observed. In the solid state, the molecule assumes an approximate boat-chair conformation with transannular S···N distances of 2.94 and 2.99 Å. This weak interaction of electrostatic nature is also present in solution. In $CDCl_3$ and $C_6D_6$ i.r. and n.m.r. experiments are in agreement with the existence of an enantiomeric equilibrium of two isoenergetic boat-chair forms involving a pseudorotational path.

EIGHT-MEMBERED heterocyclic compounds of general formula (1) have been the subject of numerous structural studies.[1-17] They display interesting problems like



X = O, S, N; Y = O, S
A = Si, Ge, Sn, As, P, Sb
Z, Z′ = H, Cl, OR, lone pair

(1)

the conformation of the ring, the geometry around the main atom A, and 1,5-interactions between the heteroatoms A and X. These transannular interactions may involve either a covalent bond or a weaker bond of electrostatic character. Thus, information may be obtained about the electrophilicity of atom A and, also, about the reaction path for nucleophilic attack.[18]

The studies so far are for compounds in which A is from Groups IV and V, *i.e.* A = Si, Ge, Sn, P, As, or Sb. To our knowledge, no structural study has been carried out in which A is from Group VI. In the present paper, the structure of the eight-membered imido-sulphite (1; A = S, X = $NCH_3$, Y = O, Z = 2,4,6-trichlorophenylimino, Z′ = lone pair) is reported. Until now, only a few compounds containing trico-ordinated sulphur have been reported and the first cyclic derivations were synthesised in 1979.[19,20] Solid state *X*-ray diffraction studies and spectroscopic investigations in solution by i.r. and n.m.r. at 250 MHz are reported here.

## EXPERIMENTAL

2-(2,4,6-Trichlorophenylimino)perhydro-1,3,2,6-dioxathiazocine was synthesised following ref. 1 and recrystallized from ethanol.

*Crystal Data.*—$C_{11}H_{13}Cl_3N_2O_2S$, $M$ = 343.6, triclinic, $P\bar{1}$, $a$ = 10.725(4), $b$ = 11.730(2), $c$ = 12.451(3) Å, $\alpha$ = 108.15(8), $\beta$ = 92.92(7), $\gamma$ = 93.50(7)°, $U$ = 1481 Å$^3$, $D_m$ = 1.52(3), $D_c$ = 1.54 g cm$^{-3}$, $Z$ = 4.

The intensity data where collected from a specimen of approximate dimensions 0.32 × 0.30 × 0.28 mm on a CAD4 Enraf–Nonius automatic diffractometer employing a $\theta$–$2\theta$ scan up to a maximum Bragg angle of 28° using Mo-$K_\alpha$ radiation and a scan angle of $0.95 + 0.347 \tan\theta$. Of the 6 614 reflections measured in this range, 5 627 independent reflections were used in the initial stages of the analysis. 5 024 reflections having $I > 3\sigma(I)$ were used in the final refinement cycles.

A periodic check of four standard reflections showed a continuous decrease of 5% in intensity and the whole set of data was corrected. The intensities of selected reflections were also corrected for Lorentz and polarization factors, and for absorption.

Atomic scattering factors of Cromer and Waber for the non-hydrogen atoms and those of Stewart *et al.* for the spherical hydrogen atoms were used. Real and imaginary dispersion corrections given by Cromer were applied for chlorine and sulphur atoms.

*Solutions and Refinement.*—Direct methods were used to solve the structure (Multan 1978) which was refined by full-matrix least-squares techniques. All non-hydrogen atoms were allowed to refine with anisotropic thermal parameters: the unweighted and weighted residuals $R$ and $R_w$ were reduced to 0.0486 and 0.0543, respectively, with $R = \Sigma|kF_o - |F_c||/\Sigma kF_o$ and $R_w = [\Sigma w^2(kF_o - |F_c|)^2/w^2k^2F_o^2]^{\frac{1}{2}}$. A difference Fourier map and an *a priori* calculation allowed the positions of the hydrogen atoms to be determined. The hydrogen atoms were assigned the fixed isotropic thermal parameter $B_H = 1.2\ B(\text{eq.C})$Å$^2$ where $B$(eq. C) is the isotropic equivalent temperature factor of the carbon to which they were bonded. A final difference Fourier map had shown no peaks greater than 0.2 eÅ$^{-3}$.

## RESULTS AND DISCUSSION

Interatomic distances and angles are listed in Tables 1 and 2. Temperature factors, structure factors, and all structural parameters are in Supplementary Publication No. SUP 23133 (30 pp.).* Figure 1 shows a perspective view of the two independent molecules (without hydrogen atoms) and the labelled schematic representation of the compound. The equations of the mean planes and the deviations of the atoms from these planes are given in Table 3. Examination of Tables 1—3 shows that the two

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1980, Index Issue.

TABLE 1

Bond lengths (Å)

| | | | |
|---|---|---|---|
| Cl(1)–C(12) | 1.731(3) | Cl(51)–C(62) | 1.729(3) |
| Cl(2)–C(14) | 1.730(3) | Cl(52)–C(64) | 1.730(3) |
| Cl(3)–C(16) | 1.728(3) | Cl(53)–C(66) | 1.727(3) |
| S(2)–N(9) | 1.518(2) | S(52)–N(59) | 1.516(2) |
| S(2)–O(1) | 1.624(2) | S(52)–O(51) | 1.635(2) |
| S(2)–O(3) | 1.634(2) | S(52)–O(53) | 1.626(2) |
| O(1)–C(8) | 1.444(4) | O(51)–C(58) | 1.423(4) |
| O(3)–C(4) | 1.407(4) | O(53)–C(54) | 1.465(4) |
| N(6)–C(5) | 1.445(4) | N(56)–C(55) | 1.477(4) |
| N(6)–C(7) | 1.461(4) | N(56)–C(57) | 1.446(4) |
| N(6)–C(10) | 1.456(4) | N(56)–C(60) | 1.460(4) |
| N(9)–C(11) | 1.404(3) | N(59)–C(61) | 1.404(3) |
| C(4)–C(5) | 1.464(4) | C(54)–C(55) | 1.499(4) |
| C(7)–C(8) | 1.495(5) | C(57)–C(58) | 1.493(4) |
| C(11)–C(12) | 1.394(4) | C(61)–C(62) | 1.401(4) |
| C(12)–C(13) | 1.383(4) | C(62)–C(63) | 1.385(4) |
| C(13)–C(14) | 1.392(4) | C(63)–C(64) | 1.373(4) |
| C(14)–C(15) | 1.378(4) | C(64)–C(65) | 1.390(4) |
| C(15)–C(16) | 1.385(4) | C(65)–C(66) | 1.389(4) |
| C(16)–C(11) | 1.398(4) | C(66)–C(61) | 1.393(4) |

TABLE 2

Selected bond angles (°)

| | | | |
|---|---|---|---|
| C(11)–N(9)–S(2) | 125.9(2) | C(61)–N(59)–S(52) | 127.6(2) |
| N(9)–S(2)–O(1) | 108.8(1) | N(59)–S(52)–O(51) | 104.6(1) |
| N(9)–S(2)–O(3) | 105.2(1) | N(59)–S(52)–O(53) | 109.1(1) |
| O(1)–S(2)–O(3) | 96.1(1) | O(51)–S(52)–O(53) | 96.8(1) |
| S(2)–O(1)–C(8) | 115.2(2) | S(52)–O(51)–C(58) | 122.2(2) |
| O(1)–C(8)–C(7) | 111.3(3) | O(51)–C(58)–C(57) | 115.6(2) |
| C(8)–C(7)–N(6) | 109.6(3) | C(58)–C(57)–N(56) | 113.8(3) |
| C(7)–N(6)–C(5) | 114.6(2) | C(57)–N(56)–C(55) | 114.4(3) |
| C(7)–N(6)–C(10) | 113.2(3) | C(57)–N(56)–C(60) | 110.1(2) |
| C(5)–N(6)–C(10) | 110.7(3) | C(55)–N(56)–C(60) | 112.1(2) |
| N(6)–C(5)–C(4) | 114.1(3) | N(56)–C(55)–C(54) | 110.0(3) |
| C(5)–C(4)–O(3) | 118.2(2) | C(55)–C(54)–O(53) | 110.3(3) |
| C(4)–O(3)–S(2) | 122.4(2) | C(54)–O(53)–S(52) | 115.7(2) |
| N(9)–S(2)–N(6) | 179.5(1) | | |

crystallographic independent molecules are closely symmetrical and almost optical isomers. Thus, the discussion of the conformation applies to only one of these molecules. Nevertheless, the lack of a crystallographic plane of symmetry involves slight differences between the two molecules.

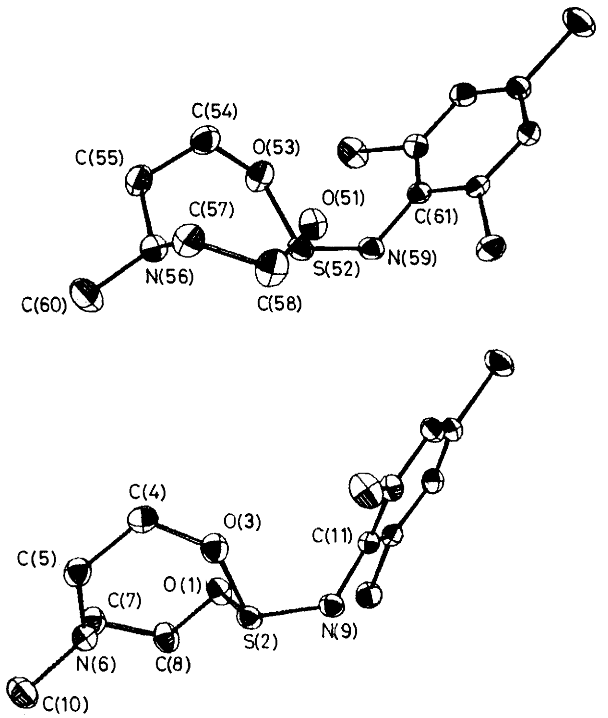



FIGURE 1 Perspective view of the two independent molecules of 2-(2,4,6-trichlorophenylimino)perhydro-1,3,2,6-dioxathiazocine

*Conformation of the Ring.*—Generally, eight-membered cyclic esters have conformations close to the canonical shapes of cyclo-octane, crown (C), chair-chair (CC), boat-boat (BB), and boat-chair (BC). In the case of

TABLE 3

Mean planes

1A C(11)–N(9)–S(2)
$$-0.814\,54x + 0.366\,23y - 0.449\,90z + 1.400\,93 = 0$$
2A O(1)–O(3)–N(9)
$$-0.455\,00x + 0.153\,35y + 0.877\,18z + 0.203\,33 = 0$$
3A S(2)–O(3)–N(6)–C(5)
$$-0.944\,91x + 0.011\,75y + 0.327\,12z + 2.244\,84 = 0$$
4A S(2)–O(1)–N(6)–C(7)
$$-0.555\,80x - 0.485\,25y + 0.872\,61z + 1.175\,53 = 0$$

1B C(61)–N(59)–S(52)
$$-0.894\,26x - 0.419\,23y + 0.156\,66z + 1.164\,33 = 0$$
2B O(51)–O(53)–N(59)
$$0.134\,94x + 0.056\,42y + 0.989\,25z - 7.416\,30 = 0$$
3B S(52)–O(53)–N(56)–C(55)
$$0.270\,99x + 0.534\,43y - 0.800\,60z + 4.470\,12 = 0$$
4B S(52)–O(51)–N(56)–C(57)
$$-0.774\,65x + 0.044\,13y - 0.630\,85z + 5.983\,91 = 0$$

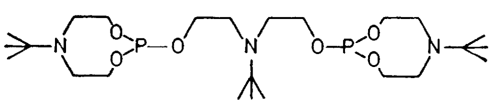
Deviations of the atoms from mean planes (Å)

| | 1A | 2A | 3A | 4A | | 1B | 2B | 3B | 4B |
|---|---|---|---|---|---|---|---|---|---|
| C(11) | 0 | −1.38 | −0.88 | −0.68 | C(51) | 0 | −1.37 | 0.81 | 0.88 |
| N(9) | 0 | 0 | 0.01 | 0.23 | N(58) | 0 | 0 | −0.07 | −0.02 |
| S(2) | 0 | 0.67 | 0.01 | 0.13 | S(52) | 0 | 0.67 | −0.06 | −0.01 |
| O(1) | −1.20 | 0 | −1.49 | −0.08 | O(51) | −1.28 | 0 | 1.45 | 0.01 |
| O(3) | 1.22 | 0 | −0.01 | −1.38 | O(53) | 1.15 | 0 | 0.08 | 1.49 |
| C(4) | 1.23 | −0.08 | −0.54 | −2.06 | C(54) | 1.93 | 0.93 | −0.74 | 1.56 |
| C(8) | −1.97 | 0.93 | −1.57 | 0.69 | C(58) | −1.32 | −0.13 | 2.08 | 0.60 |
| C(5) | 1.14 | 1.16 | 0.01 | −1.43 | C(55) | 1.20 | 1.24 | −0.07 | 1.36 |
| C(7) | −1.29 | 1.30 | −1.34 | 0.04 | C(57) | −1.25 | 1.15 | 1.41 | −0.01 |
| N(6) | 0.01 | 1.95 | −0.01 | −0.08 | N(56) | −0.06 | 1.93 | 0.05 | 0.01 |
| C(10) | 0.15 | 3.29 | 0.83 | 0.58 | C(60) | −0.14 | 3.22 | −0.58 | −0.74 |

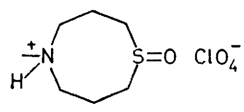
Angles between mean planes (°)

| | 1A | 2A | 3A | 4A | | 1B | 2B | 3B | 4B |
|---|---|---|---|---|---|---|---|---|---|
| 1A | | 88.2 | 51.2 | 121.7 | 1B | | 89.4 | 126.3 | 54.9 |
| 2A | | | 44.1 | 44.2 | 2B | | | 136.5 | 136.6 |
| 3A | | | | 70.6 | 3B | | | | 71.4 |

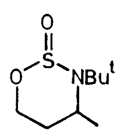
heterocycles (1), for A = Si, As, *etc.*, the A · · · X transannular interaction confers trigonal-bipyramidal geometry around A with a covalent A–X bond. This form,



(2)



(3)



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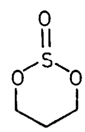

(5)

known as an atrane, is mainly of the boat-boat type.[8,9,11] Phosphorus derivatives tend to exhibit chair-chair or crown conformations.[2,6,7] However, a boat-chair form was reported, recently for the cyclic phosphite (2) [1] and previously for the sulphoxide (3).[21]

In the title compound the conformation deduced from the dihedral angles (Figure 2) and the mean planes (Table 3), is also boat-chair. The BB form is excluded for sulphur and phosphorus compounds mainly because of different hydridization and geometry around atoms A.

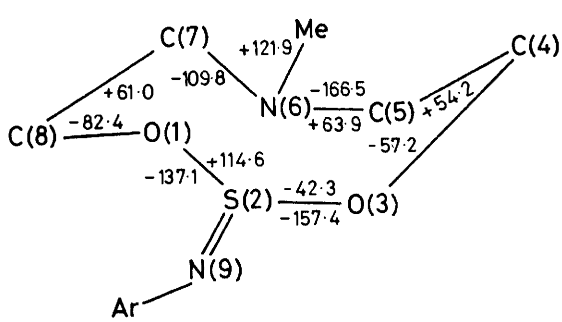


FIGURE 2 Torsion angles in one of the enantiomorphic eight-membered rings of 2-(2,4,6-trichlorophenylimino)perhydro-1,3,2,6-dioxathiazocine. The angle O(1)–S(2)–O(3)–C(4) is defined as positive if, when viewed along the S(2)–O(3) bond, O(1) must be rotated clockwise to eclipse atom C(4)

*Geometry around the Sulphur and Nitrogen Atoms*.—The sum of the angles around the sulphur atom is close to 310° which indicates a pyramidal structure for the title compound. This pyramidal structure is slightly more pronounced than in 3-t-butyl-4*c*-methyl-2*r*-oxo-1-oxa-2-thia-3-azacyclohexane (4) [22] (312°) and trimethylene sulphite (5) [23] (314°). The difference between the imido-sulphite and the sulphite lies in the O·S·O angles which are only 96.1 and 100°, respectively.

Another noticeable feature is the S·O·C angles in the title compound. An important variation of 7° is observed between them due to the dissymmetry of the BC conformation. Although less important, this phenomenon seems general for the boat-chair forms of eight-membered rings: the lowest value occurs when the S–O–C angle is located in the chair part of the ring.

Likewise, the two S–O lengths (1.62 and 1.63 Å) lie between 1.60 Å (sulphite) and 1.68 Å (sulphinamate).

Sulphur–nitrogen conjugation is of considerable current interest,[23] so the geometry around N(9) was investigated. The S(2)–N(9) bond length (1.51 Å) can be regarded as ' typical ' for an S–N double bond,[24] the S–N single bond being close to 1.65 Å;[22,24,25] moreover the phenyl ring is perpendicular to plane 1A including C(11) and the resulting rotational isomer around the S–N bond leads to maximum conjugation.

A pyramidal nitrogen atom N(6) is also observed but the pyramid is flattened compared with that of the sulphur atom: the sum of the angles around N(6) is 336.6 and 338.5° for the two pseudo-enantiomeric species.

N(6) is strictly along the axis of the S(2)–N(9) bond and at a distance of 2.94 Å from S(2). The distance S(2) · · · N(6) lies between 3.35 and 2.56 Å, values of the sums of the van der Waals radii and of the ' one angle radii ',[26,27] respectively. Similar behaviour was found recently with the cyclic phosphite (2) [1] for which the distance P · · · N is 2.87 Å. It was concluded that there was a weak interaction of electrostatic character. Indeed, *ab initio* calculations showed the existence of a potential energy well near 3 Å with a depth of *ca*. 1.1 kcal mol$^{-1}$,* and the presence of positive and negative charges on P and N respectively. It is likely that a similar explanation applies to the title compound.

Another type of transannular 1,5-interaction occurs for the sulphoxide (3) which has the same conformation as the two previously described compounds. In this case a strong hydrogen bond between oxygen and the proton linked to the nitrogen atom has been observed [21] (distances, O–N 2.65, S–N 3.25 Å). As a result, the S–O bond prefers an axial-like orientation contrary to the title compound where the S–N bond is equatorial-like.

*Conformational Analysis in Solution*.—The shape of eight-membered rings may be modified from the solid to solution as in the phosphorus series or even from one solvent to another. For instance the ring of compound (2) adopts a static crown or chair-chair form in $CDCl_3$ and a BC conformation in $C_6D_6$.[1]

I.r. and n.m.r. experiments were carried out to investigate the behaviour of the title compound. The S=N stretching vibration is assumed to be very sensitive to the conformation of the ring just as in the sulphite series [28] providing information on conformational changes. Unpublished results on six-membered cyclic imido-sulphites are consistent with this assumption. In the present case i.r. spectra were taken under various con-

* 1 cal = 4.184 J.

ditions in the 1 250—1 350 cm$^{-1}$ range where the ν(S=N) imido-sulphite band was first located by Dresdner.[29] This band was found at 1 308 cm$^{-1}$ in the solid state (KBr) and was slightly shifted to 1 303 ($CCl_4$) and 1 301 cm$^{-1}$ ($CH_3CN$) in 0.05M solutions. No temperature effect was noticed in $CS_2$ between 180 and 300 K. According to these findings no important variation in the conformation was expected which was confirmed by n.m.r. spectroscopy. $^1$H N.m.r. parameters were obtained by first-order resolution of the spectra and simulation (Table 4).

TABLE 4

$^1$H N.m.r. spectra (at 250 MHz) of 2-(2,4,6-trichlorophenylimino)perhydro-1,3,2,6-dioxathiazocine

| | Chemical shift (δ) | | | | $J_{1,3}$/ | $J_{1,4}$/ | $J_{2,3}$/ | $J_{2,4}$/ |
|---|---|---|---|---|---|---|---|---|
| Solvent | 1-H | 2-H | 3-H | 4-H | Hz | Hz | Hz | Hz |
| $CDCl_3$ | 4.44 | 4.17 | 2.89 | 2.86 | 6.4 | 3.4 | 3.9 | 6.4 |
| $C_6D_6$ | 3.89 | 3.50 | 2.10 | 1.99 | 6.8 | 3.0 | 3.4 | 6.2 |

Coupling constants of the title compound do not vary when $C_6D_6$ is substituted for $CDCl_3$ as solvent. They are closely symmetrical ($J_{1,3} \sim J_{2,4}$ and $J_{1,4} \sim J_{2,3}$) and may be explained by an enantiomeric equilibrium of two isoenergetic forms involving reasonable values of $^3J(60°)$

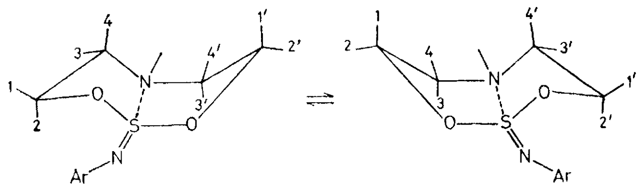

FIGURE 3 Enantiomeric equilibrium of 2-(2,4,6-trichlorophenylimino)perhydro-1,3,2,6-dioxathiazocine

(3.5 Hz) and $^3J(180°)$ (10 Hz). The interconversion process is either an inversion or a pseudorotation with twist-boat-chair (TBC) intermediates. N.m.r. low temperature experiments at 170 K in [$^2H_8$]toluene show no spectral modification. Thus, this behaviour is in agreement with the pseudo-rotational path which needs lower energy.

In conclusion, the present investigation has established that the imido-sulphite ring adopts a boat-chair conformation either in the solid state (two pairs of quasi-enantiomeric forms per unit cell) or in solution (enantiomeric equilibrium) excluding boat-boat, chair-chair, or crown conformations. This behaviour differs especially from that of cyclic phosphites in spite of *a priori* comparable 1,5-intramolecular interactions. The reasons for this peculiarity are not clear and theoretical calculations are required for a full explanation.

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REFERENCES

[1] J. Devillers, D. Houalla, J. J. Bonnet, and R. Wolf, *Nouv. J. Chim.*, 1980, **4**, 179.
[2] J. P. Dutasta, Thèse Doctorat d'Etat, University of Grenoble, 1980.
[3] J. P. Dutasta and J. B. Robert, *J. Am. Chem. Soc.*, 1978, **100**, 1925.
[4] D. Houalla, M. Sanchez, D. Goubeau, and G. Pfister-Guillouzo, *Nouv. J. Chim.*, 1979, **3**, 507.
[5] J. Martin and J. B. Robert, *Acta Crystallogr.*, 1979, **B35**, 1623.
[6] A. E. Kalinin, V. G. Andrianov, and Y. T. Stroutchkov, *Zh. Strukt. Khim.*, 1975, **16**, 1041.
[7] R. K. Sharma, K. Sampath, and R. V. Thaswamy, *J. Chem. Res.* (*S*), 1980, 12.
[8] P. Maroni, M. Holeman, and J. G. Wolf, *Bull. Soc. Chim. Belg.*, 1977, **86**, 199.
[9] P. Maroni, M. Holeman, and J. G. Wolf, *Bull. Soc. Chim. Belg.*, 1977, **86**, 209.
[10] M. Dräger, *Z. Anorg. Allg. Chem.*, 1975, **411**, 79; *Chem. Ber.*, 1974, **107**, 2601.
[11] J. J. Daly and F. Sanz, *J. Chem. Soc., Dalton Trans.*, 1974, 2051.
[12] M. Dräger, *Z. Anorg. Allg. Chem.*, 1977, **428**, 243 and references therein.
[13] M. Dräger and L. Ross, *Chem. Ber.*, 1975, **108**, 1712.
[14] M. Dräger, *Chem. Ber.*, 1975, **108**, 1723.
[15] M. Dräger and R. Engler, *Chem. Ber.*, 1975, **108**, 17.
[16] M. Dräger and R. Engler, *Z. Anorg. Allg. Chem.*, 1975, **413**, 229.
[17] M. Dräger and R. Engler, *Z. Anorg. Allg. Chem.*, 1974, **405**, 183.
[18] H. B. Bürgi, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 460.
[19] C. Picard, Thèse Docteur-Ingénieur, Toulouse, 1979.
[20] C. Picard, L. Cazaux, and P. Tisnes, *Phosphorus Sulfur*, 1981, in the press.
[21] I. C. Paul and Kuan Tee Go, *J. Chem. Soc. B*, 1969, 33.
[22] L. Cazaux, P. Tisnes, and J. Jaud, *J. Chem. Res.*, 1980, 10(S), 156(M).
[23] R. C. Haddon, S. R. Wasserman, F. Wudl, and G. R. J. Williams, *J. Am. Chem. Soc.*, 1980, **102**, 6688.
[24] A. J. Baniser and J. A. Durrant, *J. Chem. Res.* (*S*), 1978, 150.
[25] A. J. Banister and J. A. Durrant, *J. Chem. Res.* (*S*), 1978, 152.
[26] L. S. Bartell, *J. Chem. Phys.*, 1960, **32**, 827.
[27] C. Glidewell, *Inorg. Chim. Acta*, 1975, **12**, 219.
[28] L. Cazaux, J. D. Bastide, G. Chassaing, and P. Maroni, *Spectrochim. Acta, Part A*, 1979, **35**, 15.
[29] R. D. Dresdner, J. S. Johar, J. Meritt, and C. S. Patterson, *Inorg. Chem.*, 1965, **4**, 678.