124°). The changes result from experimental errors affecting the position of C(8). The mean C—C bond length in the benzene ring, not corrected for thermal motion, is 1·39 Å. Valency angles on phosphorus differ greatly: O=P—O 116, O=P—C 113, O—P—C 107 and 99, and C—P—C 108°. Some inter- and intramolecular distances are given in Table 3.

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# Structure of 2-*tert*-Butylimido-$\lambda^4$-thio-3,4-dihydro-3,3,5,8-tetramethyl-1(2*H*)-naphthalenone

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**Abstract.** $C_{18}H_{25}NOS$, monoclinic, $P2_1/c$, $a$ = 8·828 (2), $b$ = 16·916 (4), $c$ = 11·699 (3) Å, $\beta$ = 110·17 (2)°, $Z$ = 4, $d_c$ = 1·173 g cm$^{-3}$. The final $R$ = 0·044 ($R_w$ = 0·038) for the 1776 observed X-ray reflections. In the thione–imide group ($>$C=S=N—) only the S—N bond is a full double bond as indicated by the bond lengths: C—S 1·646, S—N 1·558 Å. The angle C—S—N is 110·4°. Semi-empirical calculations lead to the following charge distribution: C −0·05, S 0·44, N −0·41.

**Introduction.** The structure determination of the title compound has been undertaken in order to verify the chemical structure derived from chemical and spectroscopic studies (Crossland, 1977) and to obtain structural information on the thione–imide group. A suitable crystalline specimen was kindly supplied by Dr I. Crossland, Technical University of Denmark. From this specimen a single crystal with dimensions 0·20 × 0·13 × 0·19 mm was selected and used for data collection on a computer-controlled diffractometer (CAD-4F) with graphite-monochromatized Mo $K\alpha$ radiation. The systematic extinctions and symmetry relations among the X-ray reflections were those of the centrosymmetric space group $P2_1/c$. Unit-cell parameters with e.s.d.'s were determined by least-squares techniques from diffractometer measurements on 25 single-crystal reflections having $\theta > 10°$. 2686 independent reflections with $\theta < 24°$ were collected by the conventional $\omega$-scan technique. Of these reflections only the 1776 with $I_{\rm net}$ greater than $2\sigma(I_{\rm net})$ were considered as observed and used in the subsequent structural refinements. During the data collection a significant decay in intensities was observed for the selected reference reflections. Accordingly the collected intensities ($I_{\rm obs}$) were corrected by the function $I_{\rm corr} = I_{\rm obs}\exp(at^2 + bt)$, where $t$ is the time parameter in seconds and where the constants $a$ = 1·5 (3) × $10^{-6}$ and $b$ = 3·8 (9) × $10^{-4}$ were determined by a least-squares treatment of the intensity decay observed for

Table 1. *Fractional atomic coordinates and hydrogen atom isotropic temperature factors with e.s.d.'s*

| | *x* | *y* | *z* | *U* (Å² × 10²) |
|---|---|---|---|---|
| S | 0·3712 (1) | 0·2888 (1) | 0·6084 (1) | |
| O | 0·2973 (2) | 0·4348 (1) | 0·6967 (2) | |
| N | 0·3884 (2) | 0·2156 (2) | 0·5309 (2) | |
| C(1) | 0·1872 (3) | 0·4003 (2) | 0·6398 (2) | |
| C(2) | 0·2075 (3) | 0·3345 (2) | 0·5613 (2) | |
| C(3) | 0·0818 (3) | 0·3098 (2) | 0·4627 (2) | |
| C(4) | −0·0395 (4) | 0·3753 (2) | 0·4444 (3) | |
| C(5) | −0·2441 (3) | 0·4178 (2) | 0·5604 (3) | |
| C(6) | −0·2780 (4) | 0·4444 (2) | 0·6648 (3) | |
| C(7) | −0·1654 (4) | 0·4586 (2) | 0·7586 (3) | |
| C(8) | −0·0114 (4) | 0·4465 (2) | 0·7548 (3) | |
| C(9) | 0·0256 (3) | 0·4183 (2) | 0·6505 (3) | |
| C(0) | −0·0901 (3) | 0·4032 (2) | 0·5545 (2) | |
| C(21) | 0·5227 (3) | 0·1630 (2) | 0·5704 (3) | |
| C(22) | 0·4608 (5) | 0·0899 (3) | 0·6229 (4) | |
| C(23) | 0·5804 (5) | 0·1415 (3) | 0·4591 (4) | |
| C(24) | 0·6519 (4) | 0·2002 (2) | 0·6571 (4) | |
| C(31) | 0·1456 (5) | 0·3003 (3) | 0·3493 (3) | |
| C(32) | 0·0094 (4) | 0·2322 (2) | 0·4943 (4) | |
| C(51) | −0·3712 (4) | 0·4050 (3) | 0·4576 (4) | |
| C(81) | 0·1083 (5) | 0·4640 (3) | 0·8611 (3) | |
| H(21) | 0·4177 (38) | 0·1098 (19) | 0·6937 (31) | 8·6 (12) |
| H(22) | 0·3813 (41) | 0·0674 (19) | 0·5704 (28) | 9·4 (13) |
| H(23) | 0·5425 (35) | 0·0486 (18) | 0·6404 (24) | 7·5 (10) |
| H(24) | 0·6556 (35) | 0·1022 (18) | 0·4748 (25) | 7·8 (11) |
| H(25) | 0·4978 (37) | 0·1140 (19) | 0·4010 (29) | 9·4 (12) |
| H(26) | 0·6309 (39) | 0·1879 (20) | 0·4214 (28) | 10·2 (13) |
| H(27) | 0·7390 (31) | 0·1619 (15) | 0·6739 (21) | 5·9 (9) |
| H(28) | 0·6178 (32) | 0·2115 (17) | 0·7315 (26) | 7·6 (10) |
| H(29) | 0·6891 (33) | 0·2466 (18) | 0·6225 (25) | 7·5 (11) |
| H(31) | 0·0608 (37) | 0·2887 (18) | 0·2836 (29) | 9·1 (12) |
| H(32) | 0·2122 (37) | 0·2536 (21) | 0·3534 (28) | 8·2 (11) |
| H(33) | 0·2036 (41) | 0·3487 (20) | 0·3299 (33) | 11·5 (17) |
| H(34) | −0·0642 (34) | 0·2157 (16) | 0·4278 (25) | 6·9 (10) |
| H(35) | 0·0844 (30) | 0·1907 (16) | 0·5175 (24) | 5·4 (9) |
| H(36) | −0·0432 (33) | 0·2418 (18) | 0·5615 (24) | 6·6 (10) |
| H(41) | −0·1278 (31) | 0·3568 (15) | 0·3910 (23) | 5·6 (9) |
| H(42) | 0·0073 (30) | 0·4205 (16) | 0·4079 (22) | 5·3 (8) |
| H(51) | −0·3893 (30) | 0·3494 (20) | 0·4347 (23) | 6·8 (10) |
| H(52) | −0·4689 (38) | 0·4235 (16) | 0·4824 (24) | 7·1 (10) |
| H(53) | −0·3653 (38) | 0·4417 (19) | 0·3849 (31) | 9·9 (13) |
| H(6) | −0·3871 (32) | 0·4554 (15) | 0·6665 (21) | 5·7 (9) |
| H(7) | −0·1919 (29) | 0·4779 (16) | 0·8329 (24) | 5·6 (9) |
| H(81) | 0·1904 (46) | 0·4192 (21) | 0·8795 (35) | 12·8 (18) |
| H(82) | 0·1628 (40) | 0·5130 (22) | 0·8425 (32) | 10·2 (14) |
| H(83) | 0·0648 (35) | 0·4660 (19) | 0·9251 (27) | 7·5 (11) |

the reference reflections. The derived intensities were further corrected for Lorentz and polarization effects, but not for absorption ($\mu = 1{\cdot}88\ \mathrm{cm}^{-1}$).

The structure was solved by conventional direct methods (*MULTAN*), yielding most of the nonhydrogen atom positions. The remaining nonhydrogen atoms (as well as the H atoms) were located from difference electron density maps calculated after preliminary least-squares refinement of the structure. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). In the final least-squares refinement the unweighted linear *R* value became 0·044 and the shifts of the parameters were all below their e.s.d.'s. In this last refinement of 290 parameters *versus* the 1776 observed structure factor magnitudes, the 21 nonhydrogen atoms were kept anisotropic. The observations were weighted according to the expression $w^{-1} = a + b|F| + c|F|^2 + d \sin\theta/\lambda$, where the constants $a = 2{\cdot}39$, $b = -0{\cdot}257$, $c = 6{\cdot}66 \times 10^{-3}$ and $d = 0{\cdot}731$ were determined to give a distribution of $w|\Delta F|^2$ ($\Delta F = |F_{\rm obs}| - |F_{\rm calc}|$) which was as uniform as possible (Nielsen, 1977). The correlation coefficient obtained from a normal probability plot of the final $\sqrt{w}\Delta F$'s (Abrahams & Keve, 1971) became 0·9945 and the weighted *R* value ($R_w$) was 0·038.

Table 2. *Intramolecular bond distances* (Å) *with e.s.d.'s*

| | | | |
|---|---|---|---|
| S—N | 1·558 (3) | C(22)—H(23) | 1·00 (3) |
| S—C(2) | 1·646 (3) | C(23)—H(24) | 0·93 (3) |
| N—C(21) | 1·489 (3) | C(23)—H(25) | 1·02 (3) |
| O—C(1) | 1·225 (3) | C(23)—H(26) | 1·04 (4) |
| C(1)—C(2) | 1·473 (4) | C(24)—H(27) | 1·00 (3) |
| C(2)—C(3) | 1·512 (3) | C(24)—H(28) | 0·99 (3) |
| C(3)—C(4) | 1·529 (5) | C(24)—H(29) | 0·97 (3) |
| C(4)—C(0) | 1·511 (5) | C(31)—H(31) | 0·99 (3) |
| C(0)—C(9) | 1·402 (4) | C(31)—H(32) | 0·98 (4) |
| C(9)—C(1) | 1·486 (4) | C(31)—H(33) | 1·01 (4) |
| C(0)—C(5) | 1·395 (4) | C(32)—H(34) | 0·96 (3) |
| C(5)—C(6) | 1·383 (5) | C(32)—H(35) | 0·97 (3) |
| C(6)—C(7) | 1·366 (5) | C(32)—H(36) | 0·99 (3) |
| C(7)—C(8) | 1·383 (5) | C(4)—H(41) | 0·96 (3) |
| C(8)—C(9) | 1·402 (4) | C(4)—H(42) | 1·00 (3) |
| C(21)—C(22) | 1·525 (5) | C(51)—H(51) | 0·98 (4) |
| C(21)—C(23) | 1·523 (5) | C(51)—H(52) | 1·01 (4) |
| C(21)—C(24) | 1·522 (4) | C(51)—H(53) | 1·06 (4) |
| C(3)—C(31) | 1·538 (5) | C(6)—H(6) | 0·98 (3) |
| C(3)—C(32) | 1·533 (5) | C(7)—H(7) | 0·99 (3) |
| C(5)—C(51) | 1·509 (5) | C(81)—H(81) | 1·04 (4) |
| C(8)—C(81) | 1·512 (5) | C(81)—H(82) | 1·00 (4) |
| C(22)—H(21) | 1·03 (4) | C(81)—H(83) | 0·90 (4) |
| C(22)—H(22) | 0·93 (4) | | |

Table 3. *Intramolecular bond angles* (°) *with e.s.d.'s*

| | | | |
|---|---|---|---|
| C(2)—S—N | 110·4 (1) | C(0)—C(5)—C(6) | 117·8 (3) |
| S—N—C(21) | 116·6 (2) | C(0)—C(5)—C(51) | 121·9 (3) |
| O—C(1)—C(9) | 122·5 (3) | C(51)—C(5)—C(6) | 120·3 (3) |
| O—C(1)—C(2) | 121·8 (3) | C(5)—C(6)—C(7) | 121·8 (3) |
| C(9)—C(1)—C(2) | 115·6 (2) | C(6)—C(7)—C(8) | 121·8 (3) |
| C(1)—C(2)—C(3) | 122·1 (2) | C(7)—C(8)—C(9) | 117·4 (3) |
| S—C(2)—C(3) | 127·5 (2) | C(7)—C(8)—C(81) | 119·5 (3) |
| C(1)—C(2)—S | 110·0 (2) | C(81)—C(8)—C(9) | 123·1 (3) |
| C(2)—C(3)—C(4) | 107·9 (2) | C(8)—C(9)—C(1) | 121·2 (2) |
| C(2)—C(3)—C(31) | 110·9 (3) | C(0)—C(9)—C(1) | 118·0 (3) |
| C(2)—C(3)—C(32) | 109·5 (3) | C(8)—C(9)—C(0) | 120·7 (3) |
| C(31)—C(3)—C(4) | 108·0 (3) | C(22)—C(21)—C(23) | 110·3 (3) |
| C(31)—C(3)—C(32) | 110·5 (3) | C(22)—C(21)—C(24) | 110·2 (3) |
| C(32)—C(3)—C(4) | 110·0 (3) | C(23)—C(21)—C(24) | 110·2 (3) |
| C(3)—C(4)—C(0) | 114·3 (2) | C(22)—C(21)—N | 106·7 (3) |
| C(4)—C(0)—C(9) | 117·2 (3) | C(23)—C(21)—N | 104·2 (3) |
| C(4)—C(0)—C(5) | 122·3 (2) | C(24)—C(21)—N | 115·0 (3) |
| C(9)—C(0)—C(5) | 120·4 (3) | | |

The final structure parameters with their e.s.d.'s are listed in Table 1.* The atomic numbering is shown in Fig. 1. Bond distances, bond angles and torsion angles are in Tables 2, 3 and 4.

**Discussion.** The molecular packing is shown in Fig. 2. No intermolecular distances significantly smaller than the sum of the van der Waals radii of the atoms are found in the crystal structure. The molecular structure (*cf.* Fig. 3) can be described as mainly comprising two planar moieties through C(4)–C(0)–C(5)–C(6)–C(7)–C(8)–C(9)–C(1) and C(21)–N–S–C(2)–C(3)–C(4)···C(1). In the first case the atoms are coplanar to within 0·026 Å from a least-squares plane and in the second to within 0·069 Å. The dihedral angle between the planes is 143°. Accordingly, the six-membered ring formed by C(1)–C(2)–C(3)–C(4)–C(0)–C(9) adopts a boat-shaped conformation, as is also evident from the torsion angles listed in Table 4.

Some of the bond distances and bond angles of the benzenoid ring deviate significantly from the standard values for an unsubstituted benzene ring. Thus the C(6)–C(7) bond is only 1·366 Å and the endocyclic bond angles at the methyl-substituted C(5) and C(8) are approximately 117·5°. Most of the distances and angles of the six-membered ring system formed by C(9)–C(1)–C(2)–C(3)–C(4)–C(0) are in agreement with common standard values (Sutton, 1965). However, the bond angles at C(2) are remarkable. Since C(2) and its neighbouring atoms are coplanar, as discussed above, bond angles of about 120° would be expected. Although the endocyclic angle C(1)–C(2)–C(3) is 122·1°, the two exocyclic angles are as different as 110·0 and 127·5°. Furthermore, the intramolecular S···C(31) and S···C(32) contact distances are 3·326 and 3·376 Å while the S···O distance is as short as 2·799 Å. A plausible explanation for the large variation of the bond angles at C(2) would be steric interactions between the N atom and the methyl H atoms at C(31) and C(32), and also an interaction between the S atom and the O atom to give the shortened S···O contact. The possibility that this short contact distance is electrostatically favourable is indicated by semi-empirical calculations of atomic charges (Table 5) using CNDO methods (*cf.* Murrell & Harget, 1972), yielding opposite charges on the O and S atoms.

Table 4. *Selected torsion angles* (°) *with e.s.d.'s*

| | |
|---|---|
| C(0)–C(9)–C(1)–C(2) | −30·2 (4) |
| C(9)–C(1)–C(2)–C(3) | 24·7 (4) |
| C(1)–C(2)–C(3)–C(4) | 14·0 (4) |
| C(2)–C(3)–C(4)–C(0) | −48·4 (4) |
| C(3)–C(4)–C(0)–C(9) | 46·2 (4) |
| C(4)–C(0)–C(9)–C(1) | −4·4 (4) |
| O–C(1)–C(2)–S | 28·3 (4) |
| C(1)–C(2)–S–N | 176·1 (2) |
| C(3)–C(2)–S–N | 3·7 (3) |
| C(2)–S–N–C(21) | −173·5 (2) |

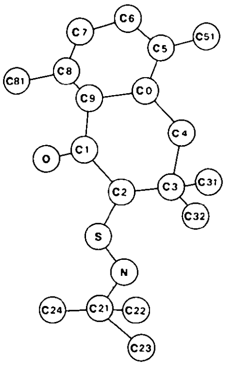

Fig. 1. Schematic structural formula of the title compound and atomic labelling used in the present study.

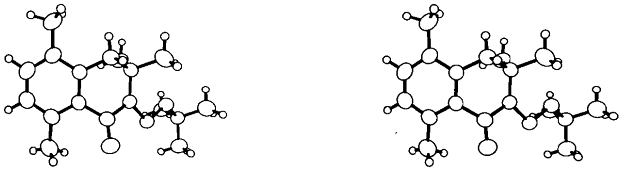

Fig. 3. The molecular geometry of the title compound. The non-hydrogen atoms are represented by their 50% thermal ellipsoids, while the H atoms are drawn with constant radii.

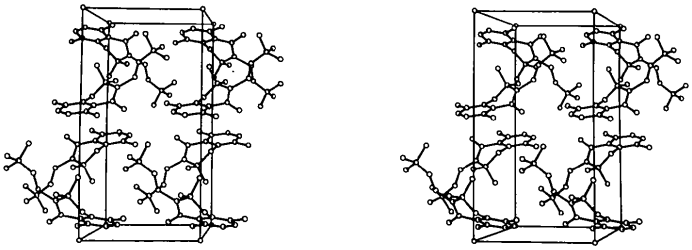

Fig. 2. Packing diagram of the crystal structure (H atoms excluded). The origin is in the lower left corner.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33623 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Atomic charges obtained from CNDO-type calculations*

| | | | | | |
|---|---|---|---|---|---|
| S | 0·44 | C(5) | 0·02 | C(22) | −0·05 |
| N | −0·41 | C(6) | −0·01 | C(23) | −0·05 |
| O | −0·39 | C(7) | −0·03 | C(24) | −0·06 |
| C(1) | 0·21 | C(8) | 0·04 | C(31) | −0·05 |
| C(2) | −0·05 | C(9) | −0·02 | C(32) | −0·05 |
| C(3) | 0·08 | C(0) | 0·02 | C(51) | −0·05 |
| C(4) | −0·02 | C(21) | 0·13 | C(81) | −0·06 |

The thione–imide group is not strictly planar, as shown by the torsion angle of 173·5° around the S—N bond. Only one of the two double bonds at the S atom is fully localized. The other is apparently delocalized over a larger fragment of the molecule. Thus the S—N bond length of 1·558 Å found in the present study is comparable to that of 1·54 Å found in $(FSN)_4$ (Wiegers & Vos, 1963), whereas the S—C bond of 1·646 Å lies between those of the single S—C bond (1·839 Å) in $(CH_2)_4S$ (Náhlovská, Náhlovský & Seip, 1969) and the double bond (1·559 Å) in $CS_2$ (Morino & Iijima, 1962). The observed S—N—C(21) bond angle is 116·6°, somewhat larger than those (about 111°) found in sulphilimine compounds (Kálmán, Sasvári & Kucsman, 1971, 1973). Because of the steric interactions between N and the methyl H atoms discussed above, the C(2)—S—N angle of 110·4° is possibly larger than expected for similar thione–imides in general.

The structural features of the thione–imide are largely in accordance with a recent structural investigation (Haagensen, 1978) of *tert*-butylimido-$\lambda^4$-thio-(phenylthio)methyl *p*-tolyl sulphone.

Thanks are due to Dr I. Crossland for supplying the crystalline material and for helpful discussions.

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# 2-Methyl-4-phenyl-2,3-butadiensäure

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**Abstract.** $C_{11}H_{10}O_2$, monoclinic, $P2_1/c$, $a = 6{\cdot}562$ (2), $b = 7{\cdot}283$ (4), $c = 20{\cdot}348$ (6) Å, $\beta = 94{\cdot}99$ (2)°, $Z = 4$, $D_x = 1{\cdot}19$ g cm$^{-3}$, $R = 0{\cdot}047$. The $\pi$ systems of the substituents are almost coplanar with the corresponding double bonds of the allene moiety. The dihedral angles between the corresponding planes are 4·2° for the carboxylic group and 14·3° for the phenyl ring.

**Einleitung.** Die Kristalle wurden durch langsames Abkühlen aus Petrolether gezüchtet. Die Gitterkonstanten haben wir aus 32 diffraktometrisch vermessenen Reflexen hoher Ordnung ($\sin\theta/\lambda \geq 0{,}51$ Å$^{-1}$) berechnet. Auf einem automatischen Einkristalldiffraktometer (AED-Siemens, Mo $K\alpha$-Strahlung, Zirkon- und Yttrium-Differenzfilter, $2\theta$–$\omega$-Abtastung) wurden bis zu einem Bereich von $\sin\theta/\lambda = 0{,}663$ Å$^{-1}$ die Intensitäten aller 2348 unabhängigen Reflexe vermessen. Davon wurden 752 als unbeobachtet angesehen [$I < 2\sigma(I)$] und erhielten anstelle von $I$ den Grenzwert $I_t = \sigma(I)$. Die Standardabweichung der Intensität $\sigma(I)$ berechnet sich aus $\sigma^2(I) = (I_{\text{brutto}} + B)$