the accuracy of our hydrogen determination hardly allows us to rule out the possibility of some departure from coplanarity.

Each molecule is connected by N–H$\cdots$O hydrogen bonds to two other molecules in head-to-tail fashion; molecules **1** and **2** alternate in the resulting infinite chains, which are parallel to **a**. The two sets of distance and angle parameters which describe the two different hydrogen bonds (Table 6) are not significantly different. Each N–H$\cdots$O bond departs significantly from linearity. The hydrogen bonding and other details of the arrangement of molecules are shown in the two stereoscopic views of Fig. 4.

Table 6. *Distance and angle parameters of the two*
hydrogen bonds

	N(1)–H$\cdots$O(2)	N(2)–H$\cdots$O(1)
N$\cdots$O	2·9001 (26)	2·9035 (27)
N–H	0·790 (21)	0·845 (24)
H$\cdots$O	2·123 (22)	2·090 (25)
N–H$\cdots$O	167·8 (2·2)	161·5 (2·5)

The interatomic distances associated with the van der Waals contacts are all in the normal range.

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The Crystal Structure of the Carotenoidal Compound 1,14-Bis-(2',6',6'-trimethylcyclohex-1'-enyl)-3,12-dimethyl-tetradeca-1,3,5,7,9,11,13-heptaene-6,9-dinitrile

BY P. B. BRAUN, J. HORNSTRA AND J. I. LEENHOUTS

Philips Research Laboratories, N. V. Philips Gloeilampenfabrieken, Eindhoven, The Netherlands

The compound crystallizes in the triclinic space group $P\bar{1}$ with $Z=1$, $a=12·79$, $b=8·58$, $c=7·36$ Å, $\alpha=101·50$, $\beta=92·11$ and $\gamma=106·96°$. Three-dimensional intensity data were collected with an automatic single-crystal diffractometer. The structure was solved using an automatic Patterson search method, assuming the conformation of a part of the molecule to be known. A least-squares refinement yielded an R_w index of 5·2%. The molecule is all-*trans* and almost straight and flat.

Introduction

The compound, $C_{36}H_{46}N_2$, m.p. 207–208°C, is one of a series of carotenoidal compounds synthesized by con-densation of polyenealdehydes with 1,4-dicyanobut-2-ene (Haeck & Kralt, 1966).

The aim of the investigation was to determine the molecular conformation, which proved to be all-*trans*.

The numbering of the atoms used throughout this paper is given in Fig. 1.

Experimental

The lattice constants and X-ray diffraction intensities of the small, irregular, dark red crystal (largest dimension 0·2 mm) were measured at room temperature. The Philips automatic single-crystal diffractometer PAILRED was used, with crystal-monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). A total of 1652 reflexions were measured: 1328 in the zero level and in 6 higher levels about [001] and 324 in the equator about [010]. The measured intensities, confined within a sphere with a radius corresponding to 1·09 Å, were corrected for Lorentz and polarization effects.

The set of independent reflexions used in the structure determination and refinement contained 1205 reflexions.
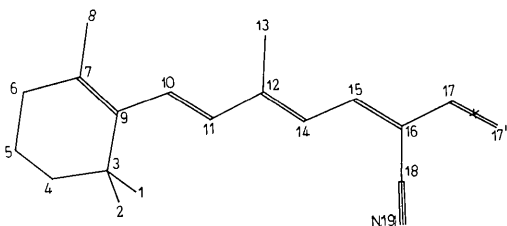

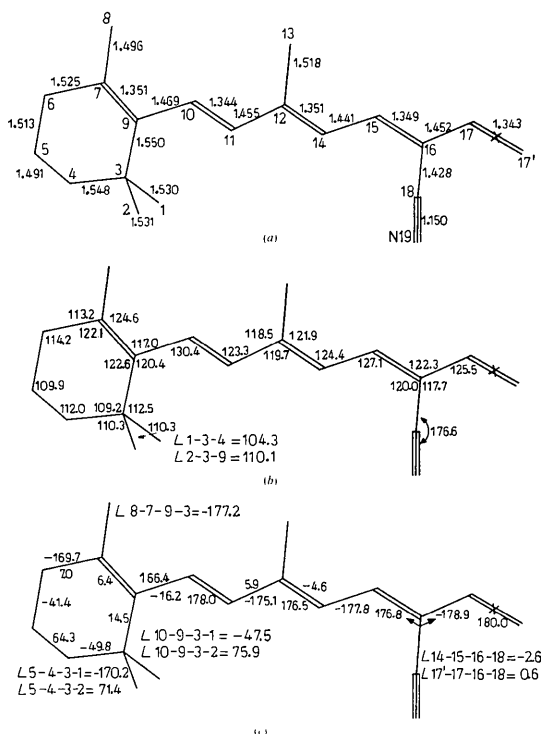Fig. 1. Numbering of the atoms as used in this paper.

Fig. 2. (a) Bond distances, mean e.s.d. = 0·007 Å, (b) bond angles, mean e.s.d. = 0·4°, and (c) dihedral angles, mean e.s.d. = 0·6°.

The crystals are triclinic with space group $P\bar{1}$ and $Z = 1$; $a = 12.79$, $b = 8.58$, $c = 7.36$ Å, $\alpha = 101.50$, $\beta = 92.11$ and $\gamma = 106.96°$.

Structure determination

The structure was solved by the automatic Patterson search method described by Braun, Hornstra & Leenhouts (1969). This method first locates the atoms contained in what is called a search model and in a second step finds the atoms not incorporated in this model. The newly developed programs for the space group $P\bar{1}$, were tried out on two structures of carotenoids with the same space group, before they were applied to the structure under investigation. The first test case, 15,15'-dehydrocanthaxanthin (Bart & MacGillavry, 1968a), with $Z = 1$ and the centre of symmetry of the molecule at the origin, showed that this structure could have been solved completely automatically. The second one, canthaxanthin (Bart & MacGillavry, 1968b), with two molecules in general positions, related by the centre of symmetry of the space group, was initially troublesome because the molecule itself is nearly centrosymmetric. After we had learned how to cope with this pseudo-symmetry in the structure (Hornstra, 1970) it could be solved automatically.

Straightforward application of the tested program to the structure on hand, with a search model containing the six-membered ring with its substituents in the same conformation as in the triclinic modification of vitamin-A acid (Stam & MacGillavry, 1963), was not successful. The least-squares refinement did not converge. Inspection of the Patterson function showed a number of high peaks, the largest of which had a magnitude equal to half that of the origin peak. From the sequence of these peaks it followed that the polyene chain is very nearly straight. Thus we concluded that a search with part of this chain as model would be very promising. We applied a model containing the molecular fragment from C(14) to C(14') with ideal bond lengths and angles, and the structure was solved without undue difficulty.

Refinement

The weighting scheme used in the least-squares refinement is described elsewhere (Braun, Hornstra & Leenhouts, 1970). The atomic scattering factors were taken from International Tables for X-ray Crystallography (1962). Before the introduction of anisotropic thermal vibration coefficients the non-hydrogen atoms were refined in a full matrix. Final refinement cycles of these C and N atoms were performed in a 9×9 block-diagonal approximation. Eleven hydrogen atoms were added at calculated positions, and the twelve hydrogen atoms of the methyl groups were located in a difference Fourier synthesis. The positional parameters of the hydrogen atoms were refined together in one matrix, while their thermal vibration coefficients were

kept equal to those of the carbon atoms to which they are bonded.

Results and accuracy

The final reliability indices are $R_w = \sum w||F_o| - k|F_c||/ \sum w|F_o| = 5.2\%$ and $\sum w\Delta^2 = \sum w(|F_o| - k|F_c|)^2 = 1694$, including all reflexions within the limiting sphere. The final difference Fourier synthesis did not show any noteworthy features.

The atomic parameters with their estimated standard deviations are given in Tables 1 and 2. These e.s.d.'s were derived from the 9×9 matrices for the C and N atoms with $m - n = 1205 - (19 \times 9 + 1) = 1033$. Those of the hydrogen atoms were obtained from the 70×70 matrix with $m - n = 1205 - 70 = 1135$.

Table 1. Positional coordinates, in fractions of the unit-cell edge with e.s.d.'s in brackets

	x	y	z
C(1)	0·33457 (47)	−0·46418 (74)	−0·94538 (74)
C(2)	0·17786 (46)	−0·51635 (74)	−1·18824 (74)
C(3)	0·29898 (42)	−0·42096 (68)	−1·12482 (65)
C(4)	0·37287 (50)	−0·47930 (78)	−1·26811 (66)
C(5)	0·36340 (50)	−0·42105 (80)	−1·44387 (78)
C(6)	0·40597 (47)	−0·23239 (80)	−1·40480 (74)
C(7)	0·37188 (38)	−0·14544 (70)	−1·22564 (62)
C(8)	0·39745 (40)	0·03896 (76)	−1·20692 (72)
C(9)	0·31886 (38)	−0·23091 (66)	−1·10350 (62)
C(10)	0·28423 (40)	−0·13428 (64)	−0·94205 (59)
C(11)	0·21446 (40)	−0·18556 (64)	−0·81855 (63)
C(12)	0·19163 (40)	−0·07200 (66)	−0·66119 (59)
C(13)	0·24054 (44)	0·11454 (67)	−0·64547 (69)
C(14)	0·12674 (41)	−0·13416 (66)	−0·53555 (64)
C(15)	0·10347 (39)	−0·03424 (65)	−0·36949 (62)
C(16)	0·04231 (40)	−0·08943 (66)	−0·23646 (62)
C(17)	0·02901 (40)	0·02310 (69)	−0·06962 (58)
C(18)	−0·01130 (41)	−0·26400 (70)	−0·25649 (64)
N(19)	−0·05920 (38)	−0·40271 (60)	−0·27081 (61)
H(1^i)	0·4174 (40)	−0·3947 (64)	−0·8826 (65)
H(1^{ii})	0·2788 (39)	−0·4469 (62)	−0·8407 (65)
H(1^{iii})	0·3390 (39)	−0·5794 (64)	−0·9647 (67)

Table 1 (cont.)

	x	y	z
H(2^i)	0·1754 (30)	−0·6380 (62)	−1·2217 (64)
H(2^{ii})	0·1362 (39)	−0·4888 (62)	−1·0927 (64)
H(2^{iii})	0·1492 (38)	−0·4864 (61)	−1·3002 (64)
H(4^i)	0·4626 (40)	−0·4240 (65)	−1·2032 (60)
H(4^{ii})	0·3505 (39)	−0·6184 (64)	−1·2970 (60)
H(5^i)	0·2813 (40)	−0·4573 (66)	−1·4902 (66)
H(5^{ii})	0·4086 (40)	−0·4686 (65)	−1·5529 (65)
H(6^i)	0·3882 (39)	−0·1767 (66)	−1·5040 (65)
H(6^{ii})	0·4835 (39)	−0·1989 (66)	−1·4094 (64)
H(8^i)	0·4512 (39)	0·0852 (63)	−1·3074 (63)
H(8^{ii})	0·3372 (39)	0·0825 (64)	−1·2175 (64)
H(8^{iii})	0·4364 (39)	0·1096 (62)	−1·0539 (64)
H(10)	0·3155 (33)	0·0009 (56)	−0·9199 (55)
H(11)	0·1713 (33)	−0·3016 (57)	−0·8280 (57)
H(13^i)	0·2240 (36)	0·1380 (58)	−0·7700 (59)
H(13^{ii})	0·2031 (37)	0·1878 (56)	−0·5612 (60)
H(13^{iii})	0·3148 (35)	0·1410 (57)	−0·6175 (59)
H(14)	0·0961 (35)	−0·2586 (57)	−0·5600 (57)
H(15)	0·1410 (34)	0·0941 (50)	−0·3406 (57)
H(17)	0·0664 (33)	0·1446 (58)	−0·0475 (56)

Molecular geometry

Bond distances, bond angles and dihedral angles for C and N are shown in Fig. 2.

The overall shape of the molecule is clearly illustrated in Fig. 3 which is a projection of the molecule on
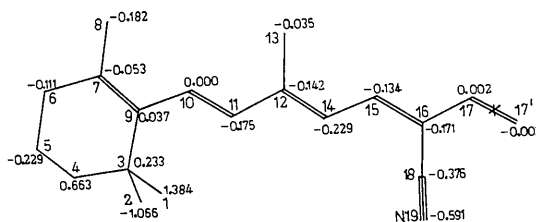

Fig. 3. Projection of the molecule on the best plane through all non-hydrogen atoms. Only half of the molecule is drawn, the other half is found by inversion through the centre of symmetry. Deviations from this plane are given in Å units.

Table 2. Anisotropic thermal vibration coefficients with e.s.d.'s in brackets

Coefficients as in the formula: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

|	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0·098 (5)	0·069 (5)	0·068 (4)	0·052 (5)	0·019 (4)	0·026 (4)
C(2)	0·078 (5)	0·060 (5)	0·068 (4)	0·015 (4)	0·009 (4)	−0·008 (4)
C(3)	0·059 (4)	0·048 (4)	0·055 (3)	0·028 (4)	0·022 (3)	0·007 (3)
C(4)	0·111 (5)	0·087 (6)	0·041 (3)	0·061 (5)	0·030 (4)	0·012 (4)
C(5)	0·102 (5)	0·084 (6)	0·073 (4)	0·052 (5)	0·044 (4)	0·011 (4)
C(6)	0·077 (5)	0·094 (6)	0·069 (4)	0·030 (5)	0·049 (4)	0·030 (4)
C(7)	0·040 (4)	0·068 (5)	0·044 (3)	0·021 (4)	0·015 (3)	0·021 (3)
C(8)	0·090 (5)	0·066 (5)	0·063 (4)	0·013 (4)	0·018 (4)	0·037 (4)
C(9)	0·040 (4)	0·047 (4)	0·046 (3)	0·014 (3)	0·014 (3)	0·006 (3)
C(10)	0·052 (4)	0·044 (4)	0·034 (3)	0·014 (3)	0·018 (3)	0·010 (3)
C(11)	0·045 (4)	0·038 (4)	0·044 (3)	0·013 (3)	0·015 (3)	0·001 (3)
C(12)	0·052 (4)	0·047 (4)	0·033 (3)	0·021 (3)	0·005 (3)	0·005 (3)
C(13)	0·068 (5)	0·042 (4)	0·061 (3)	0·024 (4)	0·020 (3)	0·005 (3)
C(14)	0·058 (5)	0·048 (4)	0·047 (3)	0·018 (4)	0·025 (3)	0·004 (3)
C(15)	0·046 (4)	0·042 (4)	0·049 (3)	0·013 (3)	0·021 (3)	0·008 (3)
C(16)	0·046 (4)	0·044 (4)	0·044 (3)	0·013 (3)	0·015 (3)	0·011 (3)
C(17)	0·052 (5)	0·045 (4)	0·035 (3)	0·011 (4)	0·014 (3)	0·008 (3)
C(18)	0·052 (4)	0·066 (4)	0·052 (3)	0·022 (4)	0·032 (3)	0·012 (3)
N(19)	0·092 (4)	0·057 (4)	0·084 (3)	0·015 (3)	0·035 (3)	0·011 (3)
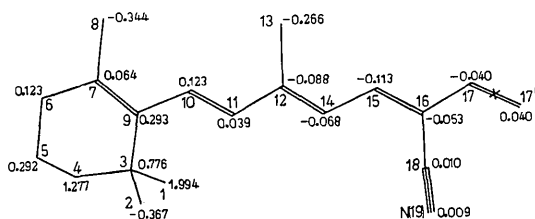
Fig. 4. Projection of the molecule on the best plane through the non-hydrogen atoms of the chain, C(10)–C(10'). Deviations from this plane are given in Å units.
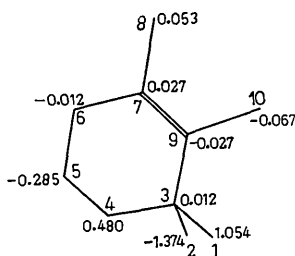

Fig. 5. Projection of the ring, with the four carbon atoms attached to it, on the best plane through the atoms C(3), C(9), C(6) and C(7). Deviations from this plane are given in Å units.

the best plane through all non-hydrogen atoms. This plane is given by the formula $0·795x - 0·300y + 0·527z = 0$ in a Cartesian reference frame in which y coincides with the b axis of the unit cell, x is along the projection of the a axis on a plane normal to y, and z is normal to x and y. Fig. 4 is a projection of the molecule on the best plane through the atoms C(10) through C(10'), i.e. the polyene chain. The equation of this plane is $0·731x - 0·475y + 0·490z = 0$; the chain is nearly straight and flat, although the deviations are significant.

Bart & MacGillavry (1968b) have compared the structures of various carotenoids. Our discussion will be developed in parallel with that review. An in-plane bending of the chain is a feature common to the various compounds discussed there. Stereochemical arguments give a well-established explanation. Although our molecule shows a straight chain, this shape may be explained by similar arguments. The angle C(11)–C(12)–C(14) is relatively small. Combined with large angles C(10)–C(11)–C(12) and C(12)–C(14)–C(15) this releases steric hindrance caused by C(13), H(10) and H(15). A bend of the chain, away from C(13) would be the result, and this is indeed found in the other structures, where it is enhanced by the presence of a second methyl group on the same side of the chain. In the

Table 3. *Shortest intermolecular distances for the half molecule*

C–C and C–N below 3·75 Å, C–H, N–H and H–H below 2·75 Å.

The following notation is used:

( )	atom at	$x' = x,$	$y' = y,$	$z' = z$
(')		$x' = -x,$	$y' = -y,$	$z' = -z$
$\pm na$		$x' \pm n$		
$\pm nb$			$y' \pm n$	
$\pm nc$				$z' \pm n$

		Distance			Distance
C(1)	C(5)+c	3·63 Å	H(4^i)	H(1$^{i'}$)+a−b−2c	2·63 Å
C(2)	N(19)−c	3·51	H(4^i)	H(5$^{ii'}$)+a−b−3c	2·69
C(5)	C(1)−c	3·63	H(4^{ii})	H(8^{ii})−b	2·70
C(8)	C(15)−c	3·74	H(4^{ii})	H(13^{ii})−b−c	2·59
C(11)	N(19')−b−c	3·71	H(4^{ii})	H(13^{iii})−b−c	2·73
C(12)	C(17')−c	3·56	H(5^i)	H(1^{ii})−c	2·60
C(13)	C(16')−c	3·62	H(5^{ii})	H(1^i)−c	2·63
C(13)	C(17')−c	3·71	H(5^{ii})	H(1^{ii})−c	2·71
C(13)	C(18')−c	3·63	H(5^{ii})	H(4$^{i'}$)+a−b−3c	2·69
C(14)	C(15')−c	3·74	H(5^{ii})	H(5$^{ii'}$)+a−b−3c	2·67
C(15)	C(8)+c	3·74	H(6^i)	H(8$^{i'}$)+a−3c	2·55
C(15)	C(14')−c	3·74	H(6^{ii})	H(8$^{i'}$)+a−3c	2·55
C(15)	C(15')−c	3·47	H(6^{ii})	H(13$^{iii'}$)+a−2c	2·46
C(16)	C(13')−c	3·62	H(8^i)	H(6$^{i'}$)+a−3c	2·55
C(17)	C(12')−c	3·56	H(8^i)	H(6$^{ii'}$)+a−3c	2·55
C(17)	C(13')−c	3·71	H(8^{ii})	H(4^{ii})+b	2·70
C(18)	C(13')−c	3·63	H(8^{ii})	H(15)−c	2·67
N(19)	C(2)+c	3·51	H(8^{iii})	H(1$^{i'}$)+a−2c	2·74
N(19)	C(11')−b−c	3·71	H(13^{ii})	H(2^i)+b+c	2·75
H(1^i)	H(4$^{i'}$)+a−b−2c	2·63	H(13^{ii})	H(4^{ii})+b+c	2·59
H(1^i)	H(5^{ii})+c	2·63	H(13^{iii})	H(4^{ii})+b+c	2·73
H(1^i)	H(8$^{iii'}$)+a−2c	2·74	H(13^{iii})	H(6$^{ii'}$)+a−2c	2·46
H(1^{ii})	H(5^i)+c	2·60	H(15)	H(2^i)+b+c	2·20
H(1^{ii})	H(5^{ii})+c	2·71	H(15)	H(8^{ii})+c	2·67
H(2^i)	H(13^{ii})−b−c	2·75	H(17)	H(2^i)+b+c	2·56
H(2^i)	H(15)−b−c	2·20			
H(2^i)	H(17)−b−c	2·56			

structure reported here, however, this effect is opposed by a similar effect on the opposite side of the chain at C(16) and by the large amount of steric hindrance of H(11) and the methyl groups C(1) and C(2), attached to the ring. As a result the deviations in the angles found here are significantly smaller and the chain is almost straight.

Fig. 5 is a projection of the ring with the four carbon atoms attached to it on the best plane through its flat part, i.e. the atoms C(3), C(9), C(6) and C(7). The equation of this plane is $0.849x - 0.201y + 0.488z = 0.4697$. The ring has the shape of a distorted half-chair and bond lengths and bond angles (Fig. 2) are in good agreement with those reported for the other carotenoids, including the short C(4)–C(5) distance.

With regard to the attachment of ring and chain, a number of interplanar angles are of interest. The angle between the overall best-plane through the chain and that through the flat part of the ring is $17.2°$. Bart & MacGillavry (1968b) computed the angle (I) between the best plane of the chain and the best plane through the double-bond system C(7)–C(9), i.e. the atoms C(3), C(9), C(10), C(7), C(6), C(8), which in our case is $16.6°$. They also tabulated the angle (II) between the best planes of the double-bond systems C(7)–C(9) and C(10)–C(11), which is $15.6°$ in the structure in question. These values are somewhat large if compared with the values of 3 and 11° reported for the only compound which, like ours, is s-trans around C(9)–C(10) but small if compared with the other cases, which have an s-cis configuration. As in the other s-trans structure, the structure reported here contains a good deal of strain in this region, as may be seen from the large deviations in the bond angles here. The angles C(3)–C(9)–C(10) and C(9)–C(10)–C(11) are very large, i.e. 120.4 and $130.4°$ respectively, whereas C(7)–C(9)–C(10) is only $117.0°$.

Remarkably enough the distance C(9)–C(10) is short (1.47 Å). The shortest H--H distances, H(8)--H(10) = 2.43, H(10)--H(13) = 2.42, H(1)--H(11) = 2.09 and H(2)--H(11) = 2.20 Å clearly illustrate the rather well balanced final situation; it is the result of two competing effects, the conjugation of ring and chain and the release of steric hindrance.

Packing

Shortest intermolecular distances, with respect to the half molecule, are listed in Table 3. Looking at the short C--C and C--N distances, it is seen that the great majority of these distances, i.e. 17 out of 19, are involved in contacts between the reference molecule and two others, at $+c$ and $-c$. This may also be seen in Fig. 6. These contacts are found over the entire length of the molecule; there exist chain-to-chain as well as chain-to-ring and ring-to-ring contacts. This suggests a description of the structure in terms of molecules packed parallel to one another, one behind the other, into bars running in the direction of the c axis. The angle between the overall plane of the molecule

and the longitudinal axis of the bar is approximately 25°.

The longitudinal axis of the chain is inclined at about 20° to the ac plane. The half molecule is found to be engaged in only two interbar contacts, both to a molecule in a bar below at $-b-c$. As a consequence the other half molecule will make contacts with the molecule at $+b+c$ in the bar above. Regarding it this way the molecule is found to be in contact with only four others.

The complete list however, i.e. including intermolecular hydrogen contacts, also exhibits contacts with molecules in bars to the right and left sides; trans-
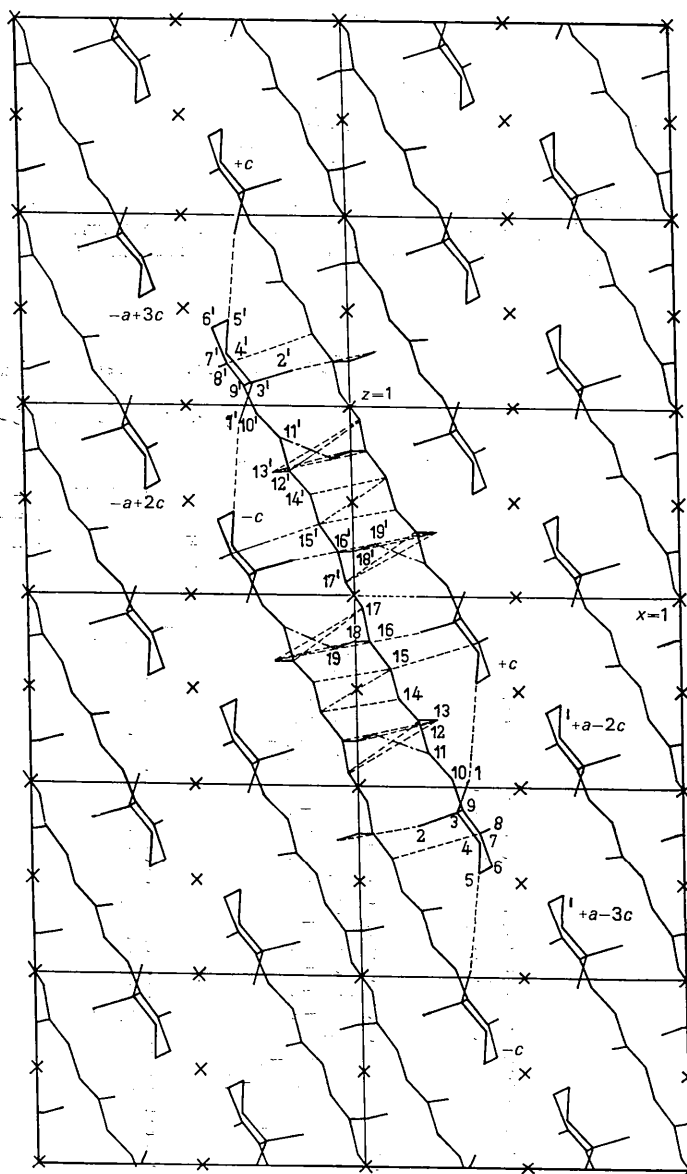

Fig. 6. Projection of the structure along [010]. Short intermolecular C–C and C–N distance are shown as ------ if intrabar, and as –·–·–· if from one bar to above and below.

lations of $+a$ and $-a$ are found. Most of these contacts are ring-to-ring, although ring-to-chain contacts do exist. Every molecule is in contact with 14 others, within the limits specified in the caption of Table 3.

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Structure Cristalline de la Molécule Schématisée par l'Équilibre Tautomère: Amino-2-phényl-5-thiazolinone-4 ⇌ Imino-2-phényl-5-thiazolidinone-4

PAR J. P. MORNON* ET B. RAVEAU§

*Laboratoire des Rayons X, IRCHA, 12, quai Henri IV, Paris 4e, France*

The compound $C_9H_8N_2OS$ (APT, IPT) crystallizes in space group $P2_1/c$ with the cell parameters $a=9\cdot30$, $b=33\cdot25$, $c=6\cdot75$ Å, $\beta=120°$, $Z=8$. The intensities were estimated from Weissenberg equi-inclination photographs and the structure determined by the symbolic addition method. The atomic parameters were refined by a least-squares method, and a final R value of $0\cdot11$ was obtained for 2145 reflexions of measurable intensity. The molecular geometry shows a delocalization of the double bond $C=N$. The contribution of the ionic forms in the resonance scheme is not negligible. The two crystallographically independent molecules form a dimer through short N---N hydrogen bonds (2·91 and 2·94 Å); this association does not occur about a symmetry centre. The crystal stability is also assured by NH---O bonds of 2·80 and 2·85 Å and by an S---O contact at 3·24 Å.

Plusieurs travaux chimiques ont eu pour objet l'étude de la tautomérie suivante:

établissent que la prépondérance de l'une ou l'autre des formes tautomères est fonction des substituants fixés

amino-2 phényl-5-thiazolinone-4 ⇌ imino-2 phényl-5-thiazolidinone-4

(APT) ⇌ (IPT)
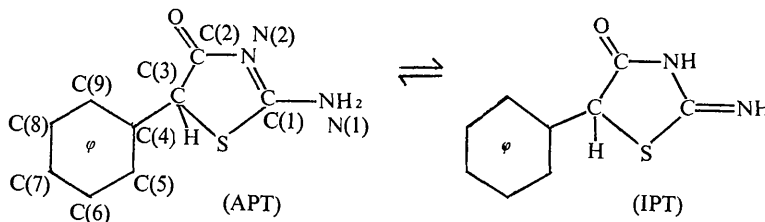
Ainsi Najer, Giudicelli, Morel & Menin (1963) étudiant les équilibres tautomères généraux:

amino-2-oxazolinone-4 ⇌ imino-2-oxazolidinone-4

et

amino-2-thiazolinone-4 ⇌ imino-2-thiazolidinone-4

sur l'atome d'azote exocyclique de façon identique pour les deux séries. Si ce substituant est un atome d'hydrogène ou un groupe alcoyle ou aralcoyle, c'est la forme amino-2 qui est prépondérante; par contre, s'il s'agit d'un groupe phényle, c'est la forme imino-2 qui prédomine. D'autre part, Reeve & Nees (1967) affirment la possibilité d'une forme zwitterion importante pour l'APT, IPT. Un travail de Comrie (1964) tente également d'apporter une réponse aux problèmes que pose la tautomérie forme amino–forme imino pour ces com-

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* Adresse présente: Laboratoire de Cristallographie, Faculté des Sciences, Tour 16, 2e étage, 9 quai St Bernard, Paris 5eme.

§ Adresse permanente: Laboratoire de Chimie Minérale II, Faculté des Sciences, 14 Caen, France.