age 1·69 ± 0·02 Å) than the aliphatic carbon–chlorine bonds (average 1·79 ± 0·01 Å). Sutton (1965) gives the average value of such vinyl bonds as 1·719 ± 0·005 Å and these aliphatic bonds as 1·767 ± 0·005 Å.

Fig. 2 shows the non-bonded chlorine···chlorine intramolecular contacts. The Cl(2)···Cl(2) (2·89 Å) and Cl(4)···Cl(4) (2·88 Å) distances are the same as the 2·89 Å chlorine···chlorine contacts in carbon tetrachloride (Bartell, Brockway & Schwendeman, 1955). The Cl(5)···Cl(6) contact (3·34 Å) is slightly longer than the value of 3·25 Å in *cis*-1,2-dichloroethane (Hoffman, 1958), as is expected. Twice the van der Waals (Pauling, 1960) radius for chlorine is 3·60 Å. Thus, the short C(1)···Cl(2), Cl(2)···Cl(3), and Cl(4)···Cl(5) distances imply repulsive interactions.

Intermolecular distances less than 4·0 Å are shown in the packing of the cell down the [010] direction, Fig. 3. There is only one kind of chlorine···chlorine contact less than twice the van der Waals radius (Pauling, 1960), the 3·51 Å contact between atoms Cl(3) and Cl(6). The molecules pack such that the Cl(6) site is above and below the centers of carbon ring systems of neighboring molecules. This situation gives rise to several short intermolecular carbon···chlorine distances. Pauling (1960) gives the effective thickness of a double-bonded carbon atom in an aromatic ring system as 3·4 Å. Thus carbon···chlorine distances of less than 3·5 Å indicate interpenetration of the electron clouds. There are no such distances in this structure.

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Structural Studies of Analgesics and Their Interactions. I. The Crystal and Molecular Structure of Antipyrine

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Antipyrine, $C_{11}H_{12}N_2O$, one of the best known pyrazole derivatives used as pain-relieving medicines, crystallizes in the monoclinic space group $C2/c$, with eight molecules in a unit cell of dimensions $a=16{\cdot}919$, $b=7{\cdot}425$, $c=17{\cdot}796$ Å and $\beta=117{\cdot}03°$. Three-dimensional intensity data from the crystal were collected on a 4-circle diffractometer. The structure was solved by the symbolic addition method and the atomic parameters, including those of the hydrogen atoms, were refined to an R value of 0·060 for 1775 reflexions. The molecular geometry of antipyrine in this structure differs substantially from that observed in some metal–antipyrine complexes. First, the differences in the dimensions of the pyrazolone ring suggest that antipyrine is considerably less polar in the free state than in the complexes. Secondly, the two nitrogen atoms in the pyrazolone ring are more pyramidal in free antipyrine than in its complexes. Consequently, the conformation of the molecule is significantly different in the two cases. The molecular structure of antipyrine is also compared with that of 3-methyl-3-pyrazolin-5-one. Antipyrine is one of the few molecules without internal symmetry which crystallize in the space group $C2/c$. The molecular packing in the structure can be most adequately described as consisting of layers of molecules parallel to the $(20\bar{4})$ plane. The molecular coordination number in this arrangement is 11.

Introduction

Several synthetic chemicals, including the derivatives of salicylic acid, pyrazole and acetanilide are extensively used as pain-relieving medicines. Most of them have varying degrees of antipyretic and anti-inflammatory properties as well. Many of these non-narcotic analgesics have been in use for several decades and a great deal of research has been carried out on their pharmacological properties when administered individually and in combination. However, the molecular basis of their interactions and their mode of action

are yet to be elucidated. A research programme of X-ray crystallographic, spectroscopic and theoretical studies on these drug molecules and their interactions among themselves and with the components of biological macromolecules has, therefore, been initiated in this laboratory (Vijayan, 1971; Singh & Vijayan, 1972). As part of the programme, the crystal and molecular structure of 1-phenyl-2,3-dimethyl-5-pyrazolone, commonly known as antipyrine, is presented here. The structures of some metallic complexes of antipyrine have already been reported from this laboratory (Vijayan & Viswamitra, 1968).

Experimental

Well developed, transparent crystals of antipyrine were grown by slow evaporation of an aqueous solution at room temperature. Examination of oscillation and Weissenberg photographs taken about crystallographic axes showed that the crystals were monoclinic, space group Cc or $C2/c$. The unit-cell dimensions obtained from X-ray photographs were refined on a Hilger and Watts 4-circle diffractometer. The density of the crystals was determined by flotation in a mixture of benzene and carbon tetrachloride.

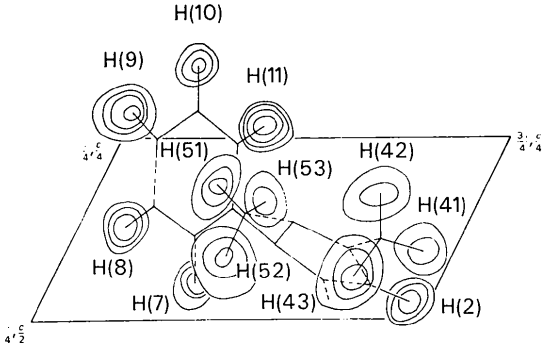

Fig. 1. Superposed sections perpendicular to the b axis of a difference Fourier map showing the positions of hydrogen atoms. The contours start at 0·2 eÅ^{-3} and are at intervals of 0·1 eÅ^{-3}.

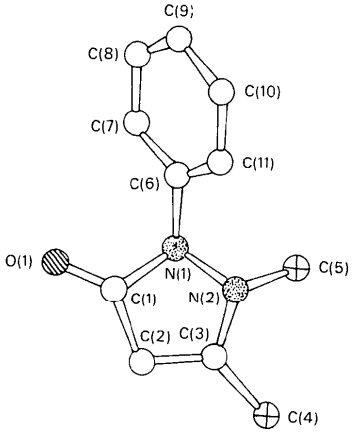

Fig. 2. A perspective view of the antipyrine molecule seen normal to the plane of the pyrazolone ring.

Crystal data

Antipyrine, $C_{11}H_{12}N_2O$.
$a = 16{\cdot}919 \pm 0{\cdot}003$, $b = 7{\cdot}425 \pm 0{\cdot}003$,
$c = 17{\cdot}796 \pm 0{\cdot}003$ Å, $\beta = 117{\cdot}03 \pm 0{\cdot}10°$, $M = 188{\cdot}112$,
$U = 1991{\cdot}247$ Å^3, $D_m = 1{\cdot}259 \pm 0{\cdot}020$ g cm^{-3}, $Z = 8$,
$D_x = 1{\cdot}255$ g cm^{-3}. Absorption coefficient for X-rays, $\lambda = 1{\cdot}5418$ Å, $\mu = 6{\cdot}75$ cm^{-1}.

Intensity data were collected on a Hilger and Watts 4-circle diffractometer belonging to Professor Dorothy Hodgkin, Laboratory of Molecular Biophysics, Oxford, from a needle-like specimen of mean radius 0·35 mm cut and ground along the b axis, up to a $\sin\theta$ limit of 0·996, using nickel-filtered copper radiation. Out of a total number of 2277 independent reflexions in the copper sphere, 2052 were accessible. Of these, 1775 reflexions measured more than three times the respective standard deviations estimated from intensity statistics. Only these were used for structure determination and refinement. The data were corrected for Lorentz–polarization but not for absorption ($\mu r = 0{\cdot}24$).

Structural analysis

The structure was solved by the symbolic addition procedure (Karle & Karle, 1966). The observed structure factors were converted into normalized structure factor amplitudes, $|E|$'s, using the scale factor and the overall temperature factor obtained from Wilson's statistics. The distribution of $|E|$'s suggested the space group to be centrosymmetric and hence $C2/c$. This was confirmed by the subsequent determination and refinement of the structure in space group $C2/c$.

Table 1. *Starting set of signs and symbols*

h	k	l	$\|E\|$	Sign or symbol	
6	6	−1	3·64	+	Origin
15	3	−7	3·06	+	
10	4	−4	3·05	A	Symbols
2	4	−14	3·49	B	
4	6	3	3·15	C	
9	5	−5	3·16	D	
3	7	1	3·73	E	
7	5	3	3·01	F	

Solution: $A = B = +$
$C = D = E = F = -$

The signs of 137 reflexions with $|E| \geq 1{\cdot}8$ could be uniquely determined by symbolic addition using a starting set of signs and symbols given in Table 1. 13 out of the 14 non-hydrogen atoms in the molecule could be easily identified from the subsequent E map. A three-dimensional Fourier synthesis phased on these atoms also revealed the position of the 14th non-hydrogen atom. The positional parameters and individual isotropic temperature factors were refined to an

R value of 0·147 on the IBM 360/44 computer at this Institute using a block-diagonal *SFLS* program originally written for the IBM 1130 computer by Dr R. Shiono and modified by Mr Swaminatha Reddy for the IBM 360/44 system. Further refinement of the structure with individual anisotropic temperature factors of the form

$$\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{23}kl+2b_{13}hl)]$$

reduced R to 0·092. A difference Fourier map (shown

Table 2. *Final positional coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^4$) *of non-hydrogen atoms*

The standard deviations are given in parentheses.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O(1)	6119 (2)	1440 (4)	4746 (2)	46 (1)	173 (6)	53 (2)	13 (2)	12 (1)	30 (2)
N(1)	5149 (2)	3723 (5)	3987 (2)	34 (1)	137 (6)	38 (1)	0 (2)	11 (1)	10 (2)
N(2)	5239 (2)	5414 (4)	3671 (2)	37 (1)	123 (6)	39 (1)	1 (2)	12 (1)	4 (2)
C(1)	5996 (3)	3001 (6)	4475 (2)	36 (2)	162 (8)	34 (2)	7 (3)	12 (1)	8 (3)
C(2)	6605 (3)	4396 (6)	4534 (3)	34 (2)	165 (8)	38 (2)	−4 (3)	9 (1)	−3 (3)
C(3)	6135 (3)	5810 (6)	4070 (3)	39 (2)	148 (7)	35 (2)	−10 (3)	13 (1)	−10 (3)
C(4)	6448 (3)	7583 (7)	3933 (3)	58 (3)	178 (9)	55 (2)	−33 (4)	19 (2)	−8 (4)
C(5)	4578 (3)	6752 (6)	3598 (3)	47 (2)	164 (9)	60 (2)	16 (3)	18 (2)	0 (4)
C(6)	4390 (2)	2664 (5)	3492 (2)	32 (1)	127 (7)	37 (2)	3 (2)	14 (1)	2 (2)
C(7)	4059 (3)	1508 (6)	3895 (3)	44 (2)	176 (8)	41 (2)	−3 (3)	20 (1)	10 (3)
C(8)	3340 (3)	417 (6)	3416 (3)	41 (2)	171 (9)	54 (2)	−2 (3)	23 (2)	15 (3)
C(9)	2945 (3)	472 (6)	2546 (3)	35 (2)	161 (8)	53 (2)	−7 (3)	18 (2)	−4 (3)
C(10)	3268 (3)	1649 (6)	2146 (3)	39 (2)	188 (9)	40 (2)	−3 (3)	15 (1)	−4 (3)
C(11)	3986 (3)	2748 (6)	2614 (3)	35 (2)	178 (8)	39 (2)	0 (3)	17 (1)	6 (3)

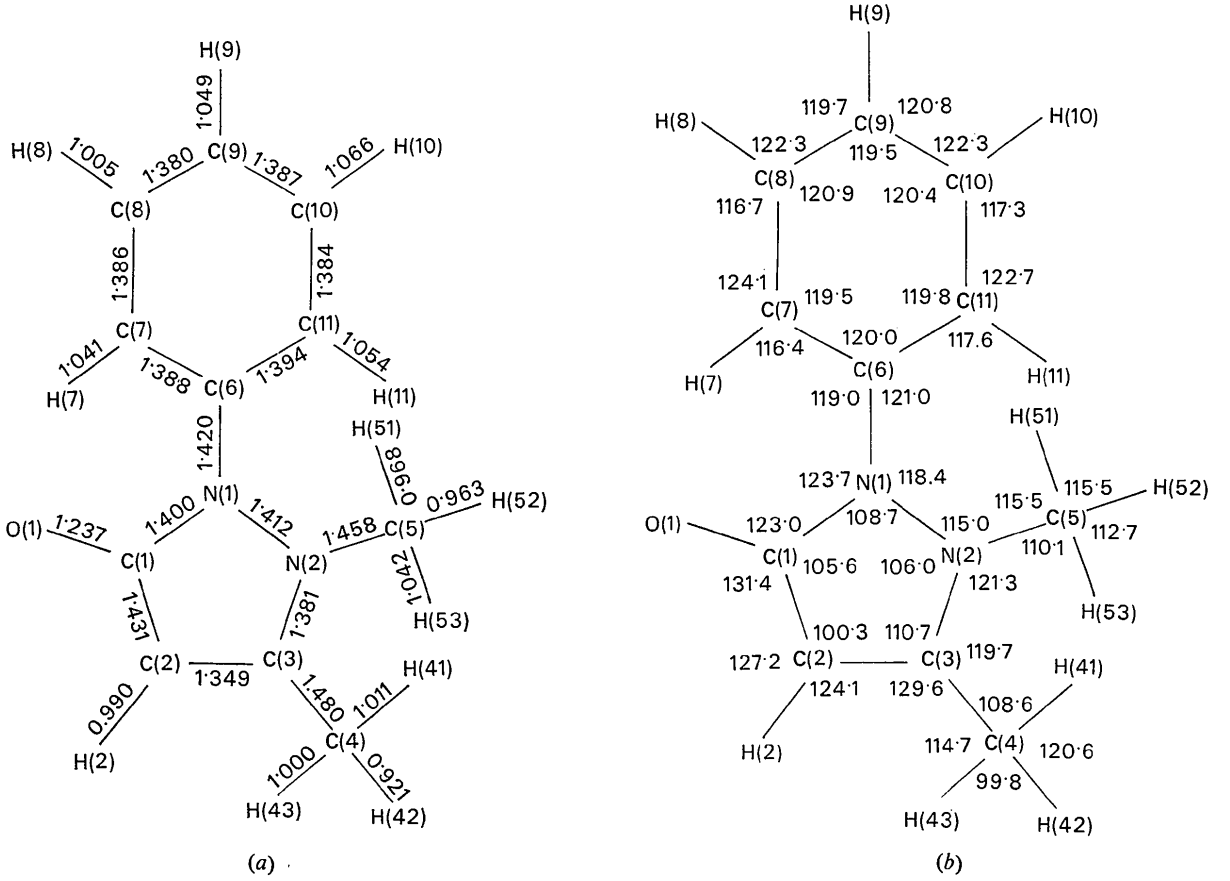

Fig. 3. (*a*) Bond lengths (Å) and (*b*) valency angles (°) in the molecule. Mean estimated standard deviations for the bond lengths are: σ(C–O) = 0·005, σ(N–N) = 0·005, σ(N–C) = 0·006, σ(C–C) = 0·007, σ(C–H) = 0·08 Å. The e.s.d.'s of bond angles involving non-hydrogen atoms vary between 0·4 and 0·5° whereas the mean e.s.d.'s of C–C–H (or N–C–H) and H–C–H angles are 3 and 5° respectively.

in Fig. 1) computed at this stage revealed the positions of all the hydrogen atoms in the structure. In subsequent *SFLS* calculations, the positional parameters and isotropic thermal parameters of the hydrogen atoms were also refined. The refinement was terminated when all the shifts indicated for the parameters of non-hydrogen atoms were less than the corresponding standard deviations, the final R value being 0·060 for 1775 observed reflexions. In the final cycle, the average and maximum shifts for the parameters of non-hydrogen atoms and hydrogen atoms were $0{\cdot}17\sigma$ and $0{\cdot}60\sigma$, and $0{\cdot}47\sigma$ and $1{\cdot}2\sigma$ respectively. The weighting function used in the final cycles had the form

$$\frac{1}{a+b(kF_o)+c(kF_o)^2}$$

where $a=1{\cdot}0$, $b=0{\cdot}1$ and $c=0{\cdot}015$ for $k=\frac{1}{2}$. In these calculations, the form factors of the non-hydrogen atoms were taken from Cromer & Waber (1965) and those of the hydrogen atoms from Stewart, Davidson & Simpson (1965). The final positional and thermal parameters of the non-hydrogen and the hydrogen atoms are listed in Tables 2 and 3 respectively. The list of observed and calculated structure factors can be obtained from the authors on request.

Table 3. *Final positional coordinates* ($\times 10^3$) *and isotropic temperature factors for hydrogen atoms*

The estimated standard deviations are given in parentheses.

	x	y	z	B
H(2)	726 (3)	432 (6)	480 (3)	3·9 (1·0)
H(41)	712 (4)	754 (7)	418 (3)	5·3 (1·2)
H(42)	610 (5)	794 (11)	358 (5)	9·6 (2·0)
H(43)	634 (4)	861 (9)	424 (4)	6·5 (1·5)
H(51)	397 (4)	648 (9)	319 (4)	6·4 (1·4)
H(52)	457 (5)	682 (9)	414 (4)	7·3 (1·6)
H(53)	472 (4)	799 (9)	341 (4)	6·6 (1·5)
H(7)	437 (4)	154 (8)	455 (3)	5·2 (1·2)
H(8)	314 (4)	−43 (7)	373 (3)	5·5 (1·2)
H(9)	241 (3)	−39 (7)	220 (3)	4·6 (1·0)
H(10)	298 (3)	175 (7)	148 (3)	4·7 (1·1)
H(11)	425 (3)	365 (6)	233 (3)	3·3 (0·9)

Discussion

Molecular geometry of antipyrine

A perspective view of the antipyrine molecule seen normal to the plane of the pyrazolone ring is shown in Fig. 2. The bond lengths and valency angles, uncorrected for thermal vibrations, are given in Fig. 3. All the lengths in the pyrazolone moiety lie between the corresponding single bond and double bond distances. The N(2)–C(5) bond is slightly, but not significantly, shorter than the accepted N–C single bond distance of 1·47 Å. However, the C(3)–C(4) distance of 1·480 ± 0·006 Å deviates substantially from the usual length (1·54 Å) of a C–C single bond. This might be due partly to the sp^2 hybridization state of C(3) (Dewar & Schmeising, 1959) and partly to the thermal vibrations of the atoms involved, especially the methyl carbon atom C(4). The dimensions of the phenyl ring are normal. The deviations of the bond lengths involving hydrogen atoms from standard values are within experimental error.

The equations of the mean planes through the phenyl ring and the pyrazolone ring were calculated using Blow's (1960) method. They were referred to a set of orthogonal axes X', Y', Z' where X' and Y' coincided with crystallographic X and Y directions and Z' was perpendicular to the XY plane. The equations and the displacements of the relevant atoms from the mean planes together with the respective standard deviations are given in Table 4. The phenyl ring is significantly planar, the atomic displacements from the plane being much less than three times the corresponding standard deviations. The deviations of the atoms in the pyrazolone ring from their mean plane are small, though significant. In the molecule, the phenyl ring and the pyrazolone ring are oriented with respect to

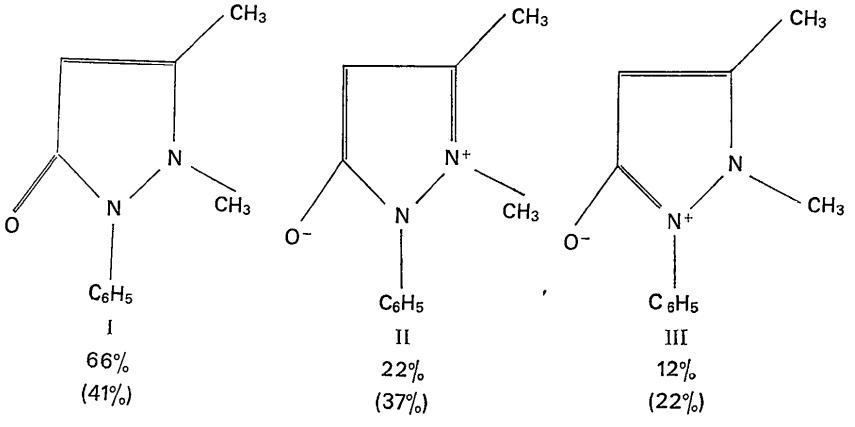

Fig. 4. Canonical structures of antipyrine and their relative contributions. The relative contributions which explain the observed bond lengths in some metallic complexes of antipyrine are given in parentheses.

each other at 52·1°. The N–C bond that connects the two rings is essentially single and hence their mutual orientation is determined by steric factors. In the structure, the carbonyl oxygen O(1) and the methyl carbon C(5) are in contact with C(7) and C(11) respectively [O(1)–C(7) = 3·106 ± 0·006 Å, C(5)–C(11) = 3·363 ± 0·006 Å]. These contacts presumably prevent the two conjugated rings from assuming a coplanar arrangement.

Table 4. *Equations of the mean planes, the displacements* (Å) *of atoms from the planes and their standard deviations* (Å)

1. Phenyl ring

$$0{\cdot}7006X' - 0{\cdot}7135Y' - 0{\cdot}0088Z' - 1{\cdot}7563 = 0$$

	Δ	σ
C(6)	0·008	0·004
C(7)	−0·005	0·005
C(8)	−0·002	0·005
C(9)	0·006	0·004
C(10)	−0·002	0·005
C(11)	−0·005	0·004

2. Pyrazolone ring

$$0{\cdot}4604X' - 0{\cdot}3958Y' - 0{\cdot}7946Z' + 3{\cdot}5445 = 0$$

	Δ	σ
N(1)	−0·046	0·003
N(2)	0·044	0·003
C(1)	0·030	0·004
C(2)	−0·002	0·004
C(3)	−0·026	0·004

Molecular dimensions in free antipyrine and in its metallic complexes

The differences between the molecular dimensions of free antipyrine determined from the present study and those observed in some metal–antipyrine complexes are significant and chemically interesting. The differences in bond lengths are best explained with reference to the three most important canonical structures (I, II and III in Fig. 4) proposed for antipyrine (Knorr, 1887; Michaelis, 1902; Kitamura, 1940; Valyashko & Bliznyukov, 1941; Brown, Hukins, Le Fèvre, Northcott & Wilson, 1949). Considering the molecule as a resonance hybrid of these three canonical forms, it is found that the observed bond lengths can be satisfactorily accounted for if the contributions from structures I, II and III are 66, 22 and 12% respectively. The bond lengths thus calculated are compared with the observed bond lengths in Fig. 5. The bond length–bond order curves used in this calculation are the same as those used earlier in the discussion of some metallic complexes of antipyrine (Vijayan & Viswamitra, 1968). A similar calculation had shown that the best fit between the observed and the calculated bond lengths of the antipyrine moiety in the complexes was obtained when the contributions of the three canonical forms were fixed at 41, 37 and 22% respectively. Thus, as expected, the effect of the association with metal ions at the carbonyl oxygen atom is to substantially enhance the contribution of the polar forms II and III. In free antipyrine, the contribution of I, which does not involve charge separation, clearly predominates. It might be pointed out that in both cases, the calculated N(1)–N(2) distance deviates considerably from its observed value. This is thought to be the consequence of the neglect of other less important canonical structures containing a N–N double bond.

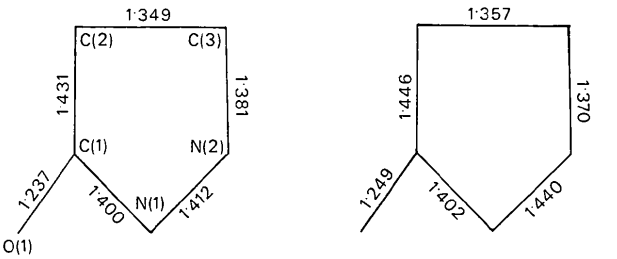

Fig. 5. (*a*) Observed and (*b*) calculated bond lengths (Å) in the pyrazolone moiety in antipyrine.

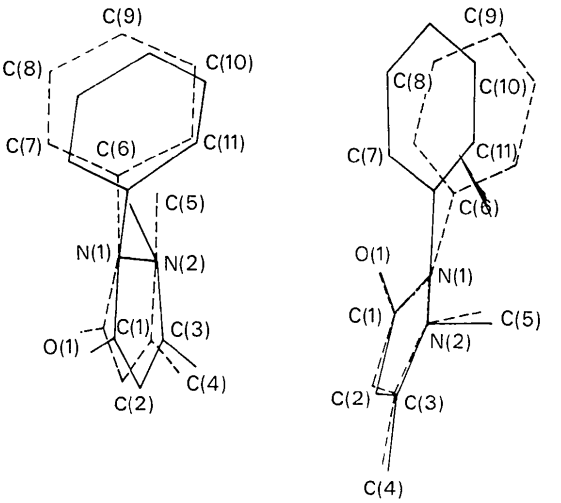

Fig. 6. Two views of the molecule in free antipyrine and its metallic complexes along comparable directions illustrating the differences in molecular conformation. The solid lines correspond to the conformation in free antipyrine and the dashed lines to that in calcium hexa-antipyrine perchlorate.

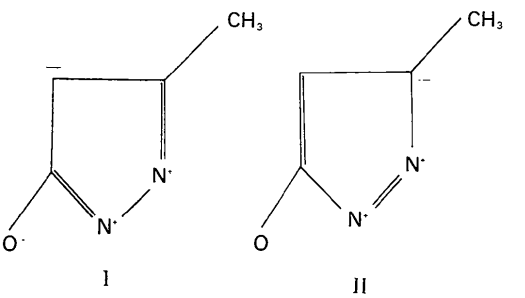

Fig. 7. Two canonical structures of MPYRAZ involving extensive charge separation.

Yet another (and somewhat unexpected) difference between the molecular geometry of antipyrine found in the present study and in the study of its metallic complexes pertains to the hybridization state of the hetero nitrogen atoms. The two nitrogen atoms are much more pyramidal in free antipyrine than in the complexes, as can be seen from the data presented in Table 5. Of the three isomorphous metal–antipyrine complexes examined earlier, the structure determination of calcium hexa-antipyrine perchlorate was the most accurate and hence the atomic parameters of the calcium compound were used in the preparation of these data. In the calcium compound, the nitrogen atoms N(1) and N(2) deviated from the planes defined by the surrounding atoms, namely C(1), C(6), N(2) and N(1), C(5), C(3), by -0.098 ± 0.011 and 0.189 ± 0.012 Å respectively, whereas the corresponding values in the present case are -0.248 ± 0.005 and 0.347 ± 0.005 Å. As a consequence, the conformation of the molecule is substantially different in the two cases. This can clearly be seen from a comparison of various dihedral angles presented in Table 6, and the views of the molecule in the two structures along comparable directions illustrated in Fig. 6. Thus a perturbation at one end of the molecule, namely the association of a metal ion with the carbonyl oxygen atom, induces strik ing changes in its overall conformation.

Table 5. *Displacements* (Å) *of some atoms from the planes of their nearest neighbours in antipyrine and calcium hexa-antipyrine perchlorate*

Estimated standard deviations are given in parentheses.

	Nearest neighbours	Δ Antipyrine	Δ Calcium compound
N(1)	C(6)N(2)C(1)	−0·247 (5)	−0·098 (11)
N(2)	C(5)N(1)C(3)	0·347 (5)	0·188 (12)
C(1)	O(1)N(1)C(2)	−0·028 (5)	−0·043 (13)
C(3)	N(2)C(4)C(2)	−0·011 (6)	0·008 (13)

Table 6. *Dihedral angles between different planes in antipyrine and calcium hexa-antipyrine perchlorate*

The estimated standard deviations for the three torsion angles calculated using the equations given by Stanford & Waser (1972) are given in parentheses.

Plane 1	Plane 2	Dihedral angles (°) Antipyrine	Calcium compound
C(6)N(1)N(2)	N(1)N(2)C(5)	66·2 (0·5)	32·7 (1·2)
C(6)N(1)C(1)	O(1)C(1)N(1)	24·7 (0·6)	5·0 (1·4)
C(5)N(2)C(3)	C(4)C(3)N(2)	41·0 (0·6)	21·9 (1·4)
Phenyl ring	Pyrazolone ring	52·1	64·7

Comparison with the structure of 3-methyl-3-pyrazolin-5-one

The crystal structures of four more pyrazolone compounds have recently become available (Smith & Barrett, 1971; De Camp & Stewart, 1970, 1971). However, the chemical structure of only one of these, namely, 3-methyl-3-pyrazolin-5-one (MPYRAZ), is directly comparable with that of antipyrine. MPYRAZ is ob-

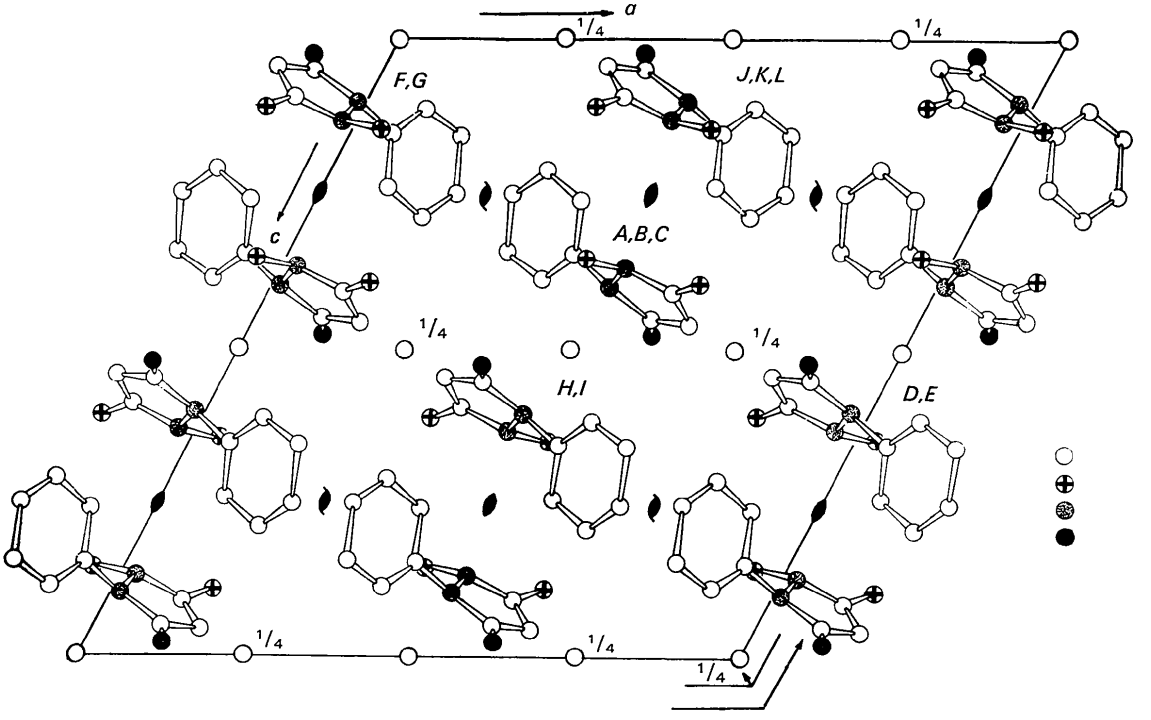

Fig. 8. The arrangement of antipyrine molecules in the unit cell. *A*: x, y, z; *B*: $x, y+1, z$; *C*: $x, y-1, z$; *D*: $\frac{1}{2}-x+1, \frac{1}{2}-y, -z+1$; *E*: $\frac{1}{2}-x+1, \frac{1}{2}-y+1, -z+1$; *F*: $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; *G*: $\frac{1}{2}-x, \frac{1}{2}+y-1, \frac{1}{2}-z$; *H*: $-x+1, -y+1, -z+1$; *I*: $-x+1, -y, -z+1$; *J*: $-x+1, y, \frac{1}{2}-z$; *K*: $-x+1, y-1, \frac{1}{2}-z$; *L*: $-x+1, y+1, \frac{1}{2}-z$.

tained by replacing the phenyl ring and the methyl group attached to the nitrogen atoms in antipyrine by hydrogen atoms. A comparison of the interatomic distances, given in Table 7, shows that the dimensions of the pyrazolone moiety are significantly different in the two compounds. Unlike those of antipyrine, the observed bond lengths in MPYRAZ cannot be explained in terms of the three canonical forms given in Fig. 4. Introduction of additional forms, like those given in Fig. 7, involving more extensive charge separation, may be required to account for the molecular dimensions of MPYRAZ.

Table 7. *Comparison of the bond lengths* (Å) *in antipyrine and 3-methyl-3-pyrazoline-5-one (MPYRAZ)*

Estimated standard deviations are given in parentheses.

	Antipyrine	MPYRAZ
C(1)–O(1)	1·237 (5)	1·285 (3)
N(1)–N(2)	1·412 (4)	1·365 (3)
N(1)–C(1)	1·400 (5)	1·337 (4)
N(2)–C(3)	1·381 (5)	1·333 (4)
C(3)–C(2)	1·349 (6)	1.357 (4)
C(2)–C(1)	1·431 (6)	1·410 (4)

Molecular packing

The arrangement of antipyrine molecules in the unit cell is illustrated in Fig. 8. All the intermolecular contact distances were calculated to a maximum limit of 4 Å. Of these, only six contacts, namely C(5)*A*–C(8)*B* (3·359 ± 0·006 Å), H(43)*A*–O(1)*B* (2·384 ± 0·07′ Å), C(8)*A*–C(5)*C* (3·359 ± 0·006 Å), O(1)*A*–H(43)*C* (2·384 ± 0·07′ Å), C(3)*A*–H(11)*J* (2·781 ± 0·040 Å) and H(11)*A*–C(3)*J* (2·781 ± 0·040 Å), have distances significantly shorter than the sum of the corresponding van der Waals radii (for the explanation of symbols *A*, *B*, ..., see the caption for Fig. 8).

According to Kitaigorodskii (1955), *C*2/*c* is not a permissible space group for molecules without internal symmetry. Antipyrine is one of the few unsymmetrical molecules which crystallize in this space group. The crystal structure, in the present case, can be most adequately described as consisting of layers of closely packed molecules parallel to the $(20\bar{4})$ plane. The molecules in each layer are related to one another by 2_1 screws (parallel to the plane of the layer), inversion centres and periodic translations along the crystallographic *b* axis, whereas adjacent layers in the structure are related to each other by twofold axes and inversion centres. Assuming two non-bonded atoms to be in contact if the corresponding interatomic distance is less than $(R_1+R_2)+0{\cdot}2A$, where R_1 and R_2 are the respective van der Waals radii, each molecule is in contact with six other surrounding molecules in the same layer, as required by the theory of Kitaigorodskii (1955). Using the same criterion, each molecule is also in contact with five more neighbours from adjacent layers, two on one side and three on the other, thus leading to a rather unusual molecular coordination number of 11 for the structure.

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