

Table 3. Bond angles ($^{\circ}$)

	Molecule A	Molecule B
C(10)–N(1)–C(2)	116.7 (1.2)	118.0 (1.1)
C(3)–C(2)–N(1)	124.4 (1.2)	122.4 (1.1)
C(4)–C(3)–C(2)	119.3 (1.4)	118.0 (1.1)
C(5)–C(4)–C(3)	116.4 (1.4)	120.6 (1.5)
C(6)–C(5)–C(4)	121.3 (1.3)	123.5 (1.4)
C(10)–C(5)–C(4)	121.4 (1.2)	117.4 (1.2)
C(10)–C(5)–C(6)	117.3 (1.4)	119.1 (1.1)
C(7)–C(6)–C(5)	120.4 (1.3)	118.8 (1.4)
C(8)–C(7)–C(6)	118.7 (1.2)	122.8 (1.1)
C(9)–C(8)–C(7)	121.1 (1.4)	119.7 (0.9)
C(10)–C(9)–C(8)	119.0 (1.3)	119.2 (1.2)
N(11)–C(9)–C(8)	122.9 (1.3)	125.0 (0.9)
N(11)–C(9)–C(10)	117.9 (1.2)	115.8 (1.0)
C(5)–C(10)–N(1)	121.8 (1.3)	123.6 (0.9)
C(9)–C(10)–N(1)	114.9 (1.2)	116.1 (1.2)
C(9)–C(10)–C(5)	123.3 (1.2)	120.3 (1.1)
S(12)–N(11)–C(9)	126.6 (0.9)	124.8 (0.7)
O(13)–S(12)–N(11)	105.1 (0.6)	107.9 (0.5)
O(14)–S(12)–N(11)	107.2 (0.5)	104.3 (0.4)
O(14)–S(12)–O(13)	119.4 (0.5)	120.5 (0.5)
C(15)–S(12)–N(11)	106.9 (0.6)	108.5 (0.5)
C(15)–S(12)–O(13)	109.6 (0.5)	105.8 (0.5)
C(15)–S(12)–O(14)	107.9 (0.5)	109.5 (0.6)
C(16)–C(15)–S(12)	118.9 (0.7)	123.0 (1.0)
C(20)–C(15)–S(12)	117.8 (0.9)	115.2 (0.9)
C(20)–C(15)–C(16)	123.3 (0.9)	121.6 (1.2)
C(17)–C(16)–C(15)	118.0 (1.0)	119.2 (1.1)
C(18)–C(17)–C(16)	120.3 (1.2)	121.3 (1.1)
C(19)–C(18)–C(17)	120.1 (1.0)	118.7 (1.5)
C(21)–C(18)–C(17)	120.6 (1.3)	120.1 (1.2)
C(21)–C(18)–C(19)	119.3 (1.1)	121.2 (1.3)
C(20)–C(19)–C(18)	120.5 (1.1)	121.5 (1.3)
C(19)–C(20)–C(15)	117.8 (1.2)	117.5 (1.1)

The chelating effect of the title molecule could be explained by the presence of the two N atoms. We shall try to confirm this point by determining the structure of a metal–LIX 34 chelate.

The molecular packing is shown in Fig. 2.

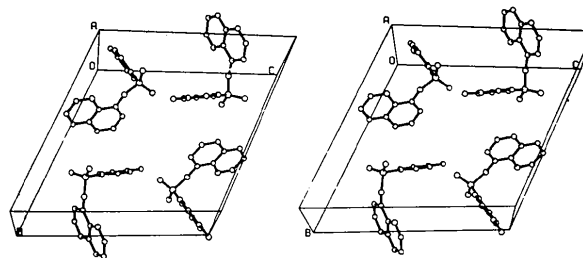


Fig. 2. Stereoscopic view of the unit cell.

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Nicotinic Acid, C₆H₅NO₂: Refinement

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Abstract. $M_r = 123.1$, monoclinic, $P2_1/c$, $a = 7.186$ (2), $b = 11.688$ (3), $c = 7.231$ (2) Å, $\beta = 113.55$ (6) $^{\circ}$, $Z = 4$. Wright & King's [*Acta Cryst.* (1953), 6, 305–317] determination of the crystal structure ($R = 0.22$) was confirmed. 6893 reflections were measured and $R(F) = 0.051$ was obtained for the 802 'observed' independent X-ray data.

Introduction. The crystal structure of nicotinic acid has already been determined by Wright & King (1953) with photographic methods ($R = 0.22$). Our reinvestigation was performed to derive more accurate parameters as a preliminary to the study of the electron density distribution in the molecule. This work is part of our project on electron density determination in derivatives

of pyridine (see also Ohms, Guth, Kutoglu & Scheringer, 1982).

Experimental. A single crystal (0.4 × 0.4 × 0.4 mm) grown from an ethanol-water solution was used to measure the integral intensities of two to four sets of symmetrically equivalent reflections up to $2\theta = 70^\circ$ (Philips automatic four-circle diffractometer, Mo $K\alpha$, graphite monochromator, $\omega-2\theta$ scan). 6893 intensities were measured altogether; the internal R values for the symmetry-equivalent reflections $[R_i(F) = \sum_{\text{ref.}} \sum_{k=1}^s |F_k - \bar{F}| / \sum_{\text{ref.}} S\bar{F}; \bar{F} = S^{-1} \sum_{k=1}^s F_k; S = \text{number of symmetry-equivalent members per reflection}]$ were $R_i(F) = 0.050$ for the observed reflections, and $R_o(F) = 0.082$ for all reflections. With $\mu = 1.2 \text{ cm}^{-1}$ an absorption correction was superfluous. After Lorentz and polarization corrections were applied, averaging over equivalent reflections yielded 3087 independent reflections, 802 of which were classified as observed [$I \geq 2\sigma(I)$]. The lattice constants were determined from the 2θ positions of 16 reflections by least-squares refinement.

The least-squares program used was written by one of us (Scheringer, 1982) and is a modification of the program described earlier (Scheringer, 1963). Scattering factors for the H, C, N and O atoms were taken from *International Tables for X-ray Crystallography* (1974). Wright & King's (1953) parameters were used as a starting set. Anisotropic thermal parameters were used except for the H atoms. Weights were taken as $w = 1/\sigma^2(F_o)$; only the observed reflections were used in the refinement. Placing the H atoms at their likely positions and refining their isotropic temperature factors (five parameters) reduced the $R(F)$ value by 0.013. A further refinement of the 15 positional parameters of the H atoms reduced the $R(F)$ value by only 0.002. The inclusion of an isotropic-extinction parameter reduced the $R(F)$ value further by 0.001. In all cases the reductions of $R(F)$ are significant at the level $\alpha = 0.005$. The same indications of significance are given when the weighted $R(F)$ values are used. With 103 parameters, we finally obtained for the 802 observed reflections the conventional R values $R(F) = 0.051$, $R_w(F) = 0.064$, goodness of fit = 0.61. The extinction parameter $g = r^* \bar{t}$ was found to be 0.0023 (6). Positional parameters and equivalent isotropic temperature factors [$B_{\text{eq}} = \frac{4}{3} \sum_{ij} \beta_{ij} g_{ij}$ (g_{ij} is the metric tensor)] are given in Table 1, † bond lengths and angles in Table 2.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38069 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters for nicotinic acid in lattice units, and isotropic temperature factors (\AA^2)*

The labelling of the atoms is the same as that of Wright & King (1953).

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} or B
C(1)	0.3517 (6)	0.2084 (3)	0.2193 (7)	2.57 (12)
C(2)	0.2602 (6)	0.3162 (3)	0.1916 (6)	2.40 (12)
C(3)	0.0510 (6)	0.3234 (3)	0.1448 (7)	2.94 (13)
C(4)	-0.0570 (6)	0.2235 (3)	0.1307 (7)	2.98 (13)
C(5)	0.0454 (6)	0.1195 (3)	0.1616 (7)	2.96 (14)
C(6)	0.3770 (6)	0.4241 (3)	0.2110 (7)	2.85 (13)
N	0.2447 (5)	0.1116 (3)	0.2040 (6)	2.93 (11)
O(1)	0.5680 (5)	0.4104 (2)	0.2431 (6)	3.86 (11)
O(2)	0.2990 (5)	0.5171 (2)	0.1999 (6)	5.00 (15)
H(1)	0.490 (5)	0.199 (3)	0.247 (5)	1.6 (3)
H(3)	-0.013 (6)	0.400 (3)	0.124 (5)	3.0 (3)
H(4)	-0.215 (6)	0.229 (3)	0.102 (6)	3.0 (3)
H(5)	-0.032 (5)	0.049 (3)	0.151 (5)	2.4 (3)
H(O)	0.648 (8)	0.466 (5)	0.257 (7)	7.9 (6)

Table 2. *Bond lengths (\AA) and bond angles ($^\circ$) in the molecule*

N-C(1)	1.348 (4)	C(5)-N-C(1)	118.9 (3)
C(1)-C(2)	1.397 (4)	N-C(1)-C(2)	121.6 (3)
C(2)-C(3)	1.406 (4)	C(1)-C(2)-C(3)	119.0 (3)
C(3)-C(4)	1.383 (5)	C(2)-C(3)-C(4)	118.8 (3)
C(4)-C(5)	1.393 (5)	C(3)-C(4)-C(5)	118.7 (3)
C(5)-N	1.342 (4)	C(4)-C(5)-N	123.0 (3)
C(2)-C(6)	1.490 (4)	C(1)-C(2)-C(6)	122.3 (3)
C(6)-O(1)	1.308 (4)	C(3)-C(2)-C(6)	118.6 (3)
C(6)-O(2)	1.211 (4)	C(2)-C(6)-O(1)	115.1 (3)
C(1)-H(1)	0.94 (4)	C(2)-C(6)-O(2)	121.7 (3)
C(3)-H(3)	0.99 (4)	O(1)-C(6)-O(2)	123.2 (3)
C(4)-H(4)	1.07 (4)		
C(5)-H(5)	0.98 (4)		
O(1)-H(O)	0.85 (5)		

Discussion. Wright & King's (1953) determination of the structure was confirmed. For the thermal parameters, Hirshfeld's (1976) rigid-bond test was calculated. For the C, N and O atoms, ΔU (bond direction) values range from 0.002 to 0.0040 \AA^2 (average 0.0017 \AA^2), which is as good as can be expected for a conventional refinement with room-temperature X-ray data. The large temperature factor for the H(O) atom, $B = 7.9 \text{ \AA}^2$, corresponds to the uncertainty with which the position of this atom in the intermolecular hydrogen bond O(1)-H(O)···N was determined. The O(1)···N distance in the hydrogen bond is 2.661 (4) \AA . The mean plane through the ring atoms was determined (Scheringer, 1971). The average displacement of these atoms from the plane was 0.0031 (14) \AA ; the maximum displacement was 0.0051 (15) \AA [C(3)]. The three remaining non-hydrogen atoms, C(6), O(1) and O(2), deviate 0.028 (3), 0.043 (4) and 0.122 (4) \AA , respectively, from the mean plane.

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Structural Studies of Radical Reaction Products.

I. The Structure of an Asymmetrically Substituted Diazene: 3-(*p*-Chlorophenyl)-4-(*p*-chlorophenylazo)-4-methyl-2-pentanone, C₁₈H₁₈Cl₂N₂O

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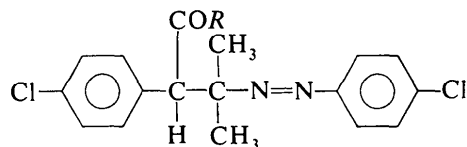
(Received 27 April 1982; accepted 21 July 1982)

Abstract. $M_r = 349.26$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 15.863$ (7), $b = 10.226$ (4), $c = 5.765$ (4) Å, $\alpha = 92.30$ (8), $\beta = 88.37$ (8), $\gamma = 108.70$ (9)° (least-squares-refined values). $U = 885.0$ (9) Å³, $D_m = 1.30$, $D_x = 1.31$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 3.71$ cm⁻¹, $F(000) = 364$. The final conventional R factor is 0.0415 for 2176 observed reflections [having $I \geq 3\sigma(I)$]. The distance between the N atoms of the azo group [1.240 (3) Å] is equal to the expected bond length between doubly bonded sp^2 -hybridized N atoms, and there is no evidence of π delocalization between the azo group and the phenyl rings. This structure proves unambiguously that aryl radical addition to a sterically hindered olefin is governed by steric factors.

Introduction. The homolytic arylation of olefins has not been extensively investigated even though significant synthetic results have been obtained using diazonium salts as the aryl radical source (Rondestedt, 1960, 1976; Citterio & Vismara, 1980).

During a systematic study of this class of reactions (Citterio, Minisci, Albinati & Brückner, 1980; Citterio, Minisci & Vismara, 1982), we have carried out an X-ray structural determination of the compound obtained from decomposition of 4-chlorobenzene-diazonium chloride by Ti^{III} ions in the presence of 4-methyl-3-penten-2-one (a sterically hindered olefin).

This product has the formula:



The formation of this compound is unexpected having been assumed, on the basis of previous work (Kellogg, 1967; Warren & Thaler, 1967; Huyser, 1970), that radicals (*e.g.* RS·, Br·, RCO·) add exclusively in the β position of olefins conjugated with electron-withdrawing groups. This structure is consistent with an aryl-group addition to the α position to the CO group and the formation of a bond between the olefinic β carbon and the β nitrogen of the diazonium ion, and demonstrates that factors affecting the regioselectivity of the reaction are related rather to steric hindrance than to resonance stabilization (Citterio *et al.*, 1980). This is in agreement with recent results of gas-phase addition of carbon radicals to olefins (Tedder & Walton, 1980), but opposite to the results obtained in solution where resonance stabilization is considered the dominant factor.

Experimental. Pale-yellow crystals with a prismatic habit and stable to air obtained by slow evaporation of