may be weak hydrogen bonds. Assuming that the positive charge in the monoprotonated biguanide is completely delocalized over the four $-NH_2$ groups, it might be expected that the N(00) lone pair of electrons would still be able to function as an acceptor in a hydrogen bond. The apparently low affinity of N(00) in $BgH^+$ for coordination with H observed here may reflect the large difference between the first and second dissociation constants (Kurzer & Pitchfork, 1968):

$$BgH^+ \rightarrow Bg + H^+ \qquad pK = 11{\cdot}5,$$

$$BgH_2^{2+} \rightarrow BgH^+ + H^+ \qquad pK = 2{\cdot}9.$$

This work was supported by the US Public Health Service, National Institutes of Health Training Grant No. GM-01728.

### References

Ernst, S. R. & Cagle, F. W. (1977). *Acta Cryst.* B**33**, 235–237.

Ernst, S. R. & Poppleton, B. J. (1974). *The Implementation of the X-RAY System of Crystallographic Programs on the DEC PDP-10 Computer.* Tech. Rep. TR-74-1. Department of Crystallography, Univ. of Pittsburgh. Pittsburgh, PA.

Fanshawe, W. J., Bauer, V. J., Ullman, E. F. & Safir, S. R. (1964). *J. Org. Chem.* **29**, 308–311.

*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP.* Oak Ridge National Laboratory Report ORNL-3794.

Kurzer, F. & Pitchfork, E. D. (1968). *Fortschr. Chem. Forsch.* **10** (3), 375–472.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The X-RAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

---

*Acta Cryst.* (1977). B**33**, 240–243

# *N*-Nitropyrazole*

By Çelik Tarimci and Ellory Schempp

*Department of Crystallography, University of Pittsburgh, Pittsburgh, PA* 15260, *USA*

(*Received* 12 *July* 1976; *accepted* 13 *August* 1976)

**Abstract.** $C_3H_3N_3O_2$, $P2_1/c$, monoclinic, $a = 7{\cdot}337\,(1)$, $b = 10{\cdot}032\,(1)$, $c = 7{\cdot}199\,(1)$ Å, $\beta = 116{\cdot}6\,(2)°$, $M_r = 113{\cdot}1$, $Z = 4$, $D_x = 1{\cdot}585$ g cm$^{-3}$. The molecule is planar and the O–N–O angle, 128·5 (2)°, is slightly larger than in other $N-NO_2$ fragments. $^{14}N$ nuclear quadrupole resonance data for several pyrazoles and 1,2,4-triazoles are listed.

**Introduction.** Five-membered N heterocycles have been studied as models of simple aromatic systems, some of which are of biological and pharmaceutical interest. Pyrazole has received repeated attention. The structure first reported by Ehrlich (1960) was later refined using neutron data by Larsen, Lehmann, Søtofte & Rasmussen (1970) and has recently been restudied with X-ray data at 295 and 108 K by La Cour & Rasmussen (1973). However, few *N*-substituted azole derivatives have been studied and we report here the structure of the only *N*-nitroazole so far prepared. This work was done in conjunction with nitrogen nuclear quadrupole resonance studies of pyrrole, pyrazole, imidazole, triazoles, and their *N*-acetyl derivatives.

$C_3H_3N_3O_2$ was prepared as described by Hüttel & Büchele (1955) by treating pyrazole nitrate with acetic anhydride. The compound is stable and melts at 93 °C without decomposition. Although it can be crystallized from high-boiling petroleum spirit, suitable crystals for X-ray studies were obtained by sublimation at 85° *in vacuo*. A crystal in the shape of a rhombic prism approximately 0·3 × 0·15 × 0·15 mm was sealed in a thin-walled capillary tube for data collection.

Oscillation and Weissenberg films showed systematic absences $h0l$, $l$ odd, and $0k0$, $k$ odd, consistent with the monoclinic space group $P2_1/c$. Data were collected at room temperature on a Picker four-circle computer-controlled diffractometer. The unit-cell parameters were refined with a routine program available for the diffractometer. Intensity data for 674 independent reflections ($\sin\theta_{max}/\lambda = 0{\cdot}556$) were collected by the $\theta/2\theta$ scan method using graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). A correction factor of

---

* This work was supported in part by a Cottrell Research Grant from the Research Corporation and by a National Science Foundation University Science Development Award, No. DID68-00431 A03.

0·02 was included in the estimated standard deviation of intensities [$\sigma^2(I) = \sigma^2(\text{scan}) + \sigma^2(\text{background}) + (0{\cdot}02\ \text{scan})^2$] to take account of instrumental fluctuations. There were 61 reflections with integrated intensity less than $2\sigma(I)$ which were considered unobserved and assigned zero weight in the refinement.

The structure was solved with the direct-method program *MULTAN* (Germain, Main & Woolfson, 1971) based on the 80 reflections with $|E| \geq 1{\cdot}5$. The resulting $E$ map gave the location of all the non-hydrogen atoms whose positions were refined first with isotropic and later with anisotropic thermal parameters by full-matrix least-squares refinement procedures with a weighting scheme based on counting statistics. Because the Fourier difference map did not reveal the H atom positions, they were initially placed at 1·0 Å along the bisectors of the appropriate angles and then refined. The final anisotropic refinement (isotropic for the H thermal parameters) resulted in an $R$ value of 0·044, including the unobserved structure factors.* The positional and thermal parameters are listed in Table 1 and the bond lengths and angles are shown in Fig. 1.

**Discussion.** The molecule is nearly planar, the ring atoms lying on the least-squares plane given by $0{\cdot}417x - 4{\cdot}641y - 5{\cdot}813z = 0{\cdot}665$ Å with a standard deviation of 0·002 Å (Fig. 2). The calculated angle between this plane and the plane of the $NO_2$ group is only 1·8° and therefore the nitro group may be considered essentially coplanar with the ring.

Comparison of the molecular geometry (Fig. 1) with that in pyrazole is difficult because, in spite of much

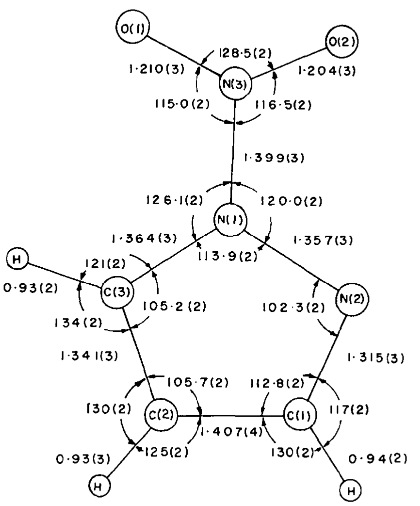

Fig. 1. Bond lengths (Å), bond angles (°), and atomic numbering in *N*-nitropyrazole.

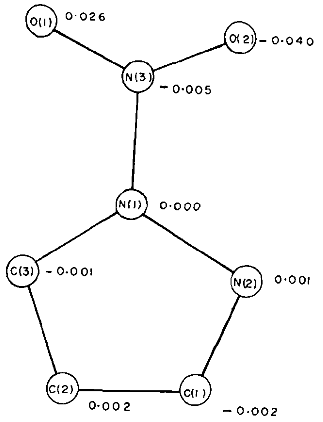

Fig. 2. Displacements (Å) from the least-squares plane through the ring N and C atoms in *N*-nitropyrazole.

Table 1. *Atomic parameters for N-nitropyrazole*

Positional parameters are given as fractions of the lattice translations. Anisotropic and isotropic temperature factors correspond, respectively, to the expressions $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ and $T = \exp(-B\sin^2\theta/\lambda^2)$. Estimated standard deviations are given in parentheses. Positional parameters for non-hydrogen atoms are × $10^4$, for hydrogen atoms × $10^3$; thermal parameters for non-hydrogen atoms are × $10^4$, for hydrogen atoms × 10.

| | $x$ | $y$ | $z$ | $U_{11}$ or $B$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 2209 (4) | −3088 (2) | 1482 (4) | 254 (8) | 106 (3) | 239 (6) | −24 (4) | 130 (6) | −2 (3) |
| C(2) | 2680 (4) | −4328 (2) | 2500 (3) | 209 (7) | 107 (3) | 215 (6) | 18 (4) | 82 (5) | −2 (3) |
| C(3) | 1007 (4) | −4694 (2) | 2678 (3) | 256 (7) | 71 (3) | 186 (6) | 6 (3) | 94 (4) | 3 (3) |
| N(1) | −362 (3) | −3690 (2) | 1777 (2) | 199 (5) | 77 (2) | 192 (5) | −4 (3) | 95 (4) | −3 (3) |
| N(2) | 351 (3) | −2684 (2) | 1023 (3) | 269 (6) | 80 (2) | 239 (5) | −8 (3) | 127 (5) | 15 (3) |
| N(3) | −2340 (3) | −3630 (2) | 1597 (3) | 217 (6) | 112 (3) | 252 (6) | −2 (3) | 105 (4) | −13 (3) |
| O(1) | −2848 (3) | −4588 (2) | 2273 (3) | 288 (6) | 130 (2) | 402 (6) | −35 (3) | 205 (5) | 10 (3) |
| O(2) | −3308 (3) | −2643 (2) | 801 (3) | 251 (6) | 144 (2) | 482 (7) | 60 (3) | 157 (5) | 53 (3) |
| H(C1) | 301 (4) | −253 (4) | 109 (4) | 34 (5) | | | | | |
| H(C2) | 392 (4) | −476 (3) | 295 (4) | 46 (6) | | | | | |
| H(C3) | 68 (4) | −542 (2) | 327 (3) | 39 (6) | | | | | |

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32028 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

study, there is still considerable uncertainty concerning the structure of pyrazole. The most recent X-ray studies of pyrazole (La Cour & Rasmussen, 1973) came to the conclusion that the two crystallographically independent molecules were identical or nearly so, both in geometry and in environment. This, however, is unlikely in view of the fact that $^{14}N$ nuclear quadrupole resonance (NQR) studies clearly show the existence of two $N_1$ sites whose quadrupole coupling constants differ by 61·7 kHz and two $N_2$ sites where the difference is 46·4 kHz (Schempp, Kruth & McCann, 1976). (The NQR studies also show that pyrazole is strongly piezoelectric.) Although these splittings can equally arise from environmental effects or from differences in the molecular bond lengths and angles, the latter is more likely since the splittings are rather large (Lucken, 1969). Hence, the assumption of identical molecules in the refinement is probably unwarranted. In any case, there are significant discrepancies, particularly in the pyrazole C(2)–C(3) bond length which has been reported as 1·361 (11), 1·346 (13), 1·369 (9), and 1·383 (10) Å, the latter two measurements by neutron diffraction. It appears that this length is somewhat shorter, 1·341 (3) Å, in N-nitropyrazole. Likewise, the N(2)–C(1) bond in the nitropyrazole, 1·315 (3) Å, seems somewhat shorter than in pyrazole, 1·325 (10) Å average. This N(2)–C(1) bond in the pyrazoles is

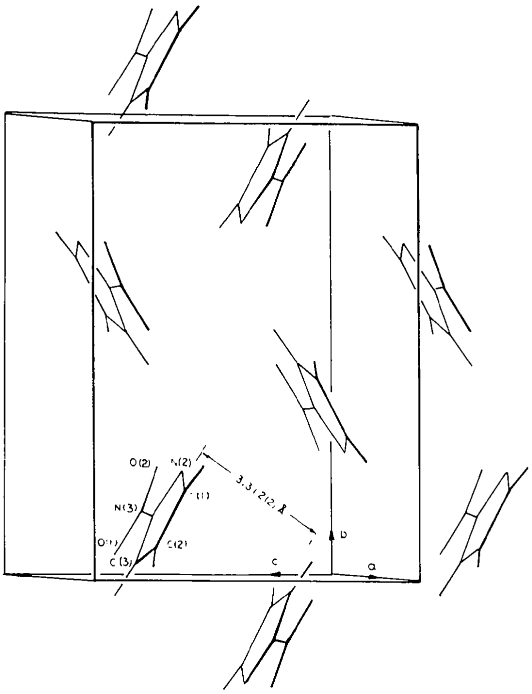

Fig. 3. Crystal packing of the *N*-nitropyrazole molecules.

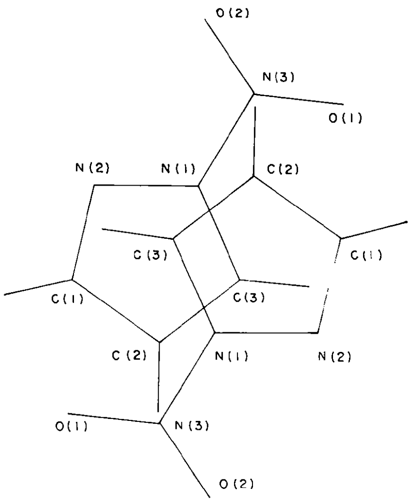

Fig. 4. Centrosymmetrically related pairs of *N*-nitropyrazole molecules viewed in projection along the directions normal to their planes.

Table 2. $^{14}N$ *nuclear quadrupole resonance frequencies,* $\nu_{\pm}$ *and* $\nu_d = \nu_+ - \nu_-$, *quadrupole coupling constants,* $e^2qQ$, *and asymmetry parameters in several pyrazoles and triazoles at* 77 K

| Compound | | $\nu_+$(kHz) | $\nu_-$(kHz) | $\nu_d$(kHz) | $e^2qQ$ | $\eta$ | References |
|---|---|---|---|---|---|---|---|
| Pyrazole | $N_1$ | 2314·9 | 1423·0 | 891·8 | 2522·8* | 0·7104* | *a,b* |
| | | 2365·3 | 1465·1 | 900·2 | | | |
| | $N_2$ | 3664·9 | 2118·2 | 1546·7 | 3832·1* | 0·8123* | |
| | | 3639·7 | 2073·8 | 1566·5 | | | |
| *N*-Acetylpyrazole | $N_1$ | 2583·6 | 1770·1 | – | 2902·5 | 0·5606 | *a,b* |
| | $N_2$ | 4095·4 | 2582·8 | 1512·2 | 4452·2 | 0·6795 | |
| *N*-Nitropyrazole† | $N_1$ | 4177·4 | 2302·9 | 1875·0 | 4320·2 | 0·8678 | *c* |
| | $N_2$ | 4076·8 | 2712·7 | 1364·3 | 4526·3 | 0·6027 | |
| 1,2,4-Triazole | $N_1$ | 2164·5 | 1538·5 | – | 2468·7 | 0·5071 | |
| | $N_2$ | 3875·9 | 2469·2 | 1407·0 | 4230·1 | 0·6651 | *a,b* |
| | $N_4$ | 2551·3 | 2778·9 | – | 3220·2 | 0·1691 | |
| *N*-Acetyl-1,2,4-Triazole | $N_1$ | 2525·3 | 1601·6 | 914·7 | 2757·3 | 0·6635 | *b* |
| | $N_2$ | 4096·5 | 2481·3 | 1615·3 | 4384·9 | 0·7368 | |
| | $N_4$ | 2974·8 | 2835·0 | – | 3873·2 | 0·0722 | |

References: (*a*) Schempp & Bray (1967). (*b*) Schempp, McCann & Kruth (1976). (*c*) This work.
* Average values. † Assignment tentative.

noticeably shorter than the N—C bond lengths in pyridines, which are about 1·340 (5) Å (Chao & Schempp, 1977).

The N(1)—C(3) and N(1)—N(2) bonds in *N*-nitropyrazole, 1·364 (3) and 1·357 (3) Å respectively, are significantly longer, by 0·03 and 0·01 Å respectively, than in the unsubstituted ring, and the C(1)—C(2) bond is also longer by about 0·02 Å. The lengthening of the bonds adjacent to the point of substitution may be attributed to the electron-withdrawing character of the nitro group which appears to diminish the double bonding of these two bonds. The bond angles show no important differences in the two compounds.

The N(1)—N(3) bond length, 1·399 (3) Å, and the O—N—O angle, 128·5 (2)°, in *N*-nitropyrazole are slightly larger than in other N—$NO_2$ fragments. In several substituted nitramines Choi & Bulusu (1974) have found N—N bond lengths averaging 1·372 (19) Å and ONO angles near 125·3 (9)°; in dimethylnitramine, $(CH_3)_2N—NO_2$, the N—N bond has been given as 1·30 Å by Allen & Sutton (1950; Table 1, entry No. 126), and in $(CH_3)_3N—N—NO_2$, the N—$NO_2$ bond length is 1·323 (8) Å with an O—N—O angle of 121·5 (6)° (Cameron, Hair & Morris, 1972).

The molecules in *N*-nitropyrazole are packed as two sets of layers oriented at 125° with respect to each other (Fig. 3). The stacking separation of the molecular planes is 3·312 (2) Å. The degree of overlap between the stacked molecules is shown in Fig. 4 where centrosymmetrically related pairs are viewed along the direction normal to the molecular planes.

### *Nuclear quadrupole resonance*

The $^{14}N$ NQR (Schempp & Bray, 1970) data in several pyrazoles and triazoles are listed in Table 2. The assignments of the lines in pyrazole differ from earlier results (Schempp & Bray, 1967) as a consequence of obtaining the complete spectrum (Schempp, Kruth & McCann, 1976). The lines reported for *N*-nitropyrazole are assigned to the N(1) and N(2) ring sites, and none of the nitro nitrogen lines has been observed, presumably because the frequencies are very low in this case (Subbarao, Sauer & Bray, 1973). Also, the lines in *N*-nitropyrazole cannot be assigned unambiguously between the N(1) and N(2) sites owing to the similarity in the values; our choice is based upon assigning the larger coupling constant to N(2) and the monotonic decrease in the asymmetry parameter of the N(2) site with increasing electronegativity of the *N*-substituent.

The Townes and Dailey semi-empirical theory for relating quadrupole resonance data to the bond populations has not proved successful in five-membered rings (Schempp & Bray, 1970; Lucken, 1969; Tarimci, 1976). Nevertheless, the large value for the quadrupole coupling constant for the N(1) site is indicative of a significant change in the electron density at N(1) from that in unsubstituted pyrazole.

### References

ALLEN, P. W. & SUTTON, L. E. (1950). *Acta Cryst.* **3**, 46–72.

CAMERON, A. F., HAIR, N. J. & MORRIS, D. G. (1972). *J. Chem. Soc. Perkin* II, pp. 1071–1076.

CHAO, M. & SCHEMPP, E. (1977). *Acta Cryst.* To be published.

CHOI, C. S. & BULUSU, S. (1974). *Acta Cryst.* **B30**, 1576–1580.

EHRLICH, H. W. W. (1960). *Acta Cryst.* **13**, 946–952.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HÜTTEL, R. & BÜCHELE, F. (1955). *Chem. Ber.* **10**, 1586–1590.

LA COUR, T. & RASMUSSEN, S. E. (1973). *Acta Chem. Scand.* **27**, 1845–1854.

LARSEN, F. K., LEHMANN, M. S., SØTOFTE, I. & RASMUSSEN, S. E. (1970). *Acta Chem. Scand.* **24**, 3248–3258.

LUCKEN, E. A. C. (1969). *Nuclear Quadrupole Coupling Constants*. New York: Academic Press.

SCHEMPP, E. & BRAY, P. J. (1967). *Phys. Lett.* **24A**, 414–416.

SCHEMPP, E. & BRAY, P. J. (1970). *Physical Chemistry*, Vol. 4, edited by D. HENDERSON. New York: Academic Press.

SCHEMPP, E., KRUTH, P. & MCCANN, M. (1976). Unpublished.

SUBBARAO, S. N., SAUER, E. G. & BRAY, P. J. (1973). *Phys. Lett.* **42A**, 461–462.

TARIMCI, Ç. (1976). Ph.D. Thesis, Univ. of Pittsburgh.