References

Brady, O. L. & Cropper, F. R. (1950). *J. Chem. Soc.* pp. 507–516.

Bucourt, R. & Hainaut, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.

Domenicano, A. & Murray-Rust, P. (1979). *Tetrahedron Lett.* **24**, 2283–2286.

Holden, J. R., Dickinson, C. & Bock, C. M. (1972). *J. Phys. Chem.* **76**, 3597–3602.

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

Kitaigorodskii, A. I. (1961). *Organic Chemical Crystallography*. New York: Consultants Bureau.

Krygowsky, T. M. (1990). *Prog. Phys. Org. Chem.* **17**, 239–291.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Maurin, J. K. & Krygowski, T. M. (1987). *Acta Cryst.* C**43**, 64–66.

Maverick, E. F. & Trueblood, K. N. (1988). *THMA11*. Univ. of California, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Norrestam, R. & Schepper, L. (1981). *Acta Chem. Scand. Ser. A*, **35**, 91–103.

Punte, G., Rivero, B. E., Socolovsky, S. & Nudelman, N. S. (1987). *Acta Cryst.* A**43**, C-169.

Punte, G., Rivero, B. E., Socolovsky, S. & Nudelman, N. S. (1989). *Acta Cryst.* C**45**, 1952–1957.

Punte, G., Rivero, B. E., Socolovsky, S. & Nudelman, N. S. (1991). *Acta Cryst.* C**47**, 1222–1227.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Zyss, J. & Tsoucaris, G. (1990). In *Structure and Properties of Molecular Crystals*, edited by M. Pierrot. Amsterdam: Elsevier.

Acta Cryst. (1991). C**47**, 2122–2124

Structure of *trans*-2,2,5,5-Tetracyano-3,6-diphenylpiperazine–Propanone (1/2)

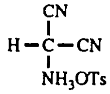
By Fillmore Freeman,* Darrick S. H. L. Kim and Joseph W. Ziller

Department of Chemistry, University of California at Irvine, Irvine, California 92717, *USA*

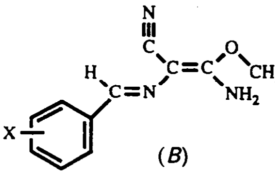
(*Received* 11 *May* 1990; *accepted* 18 *March* 1991)

Abstract. *trans*-3,6-Diphenyl-2,2,5,5-piperazinetetracarbonitrile–propanone (1/2), $C_{20}H_{14}N_6.2C_3H_6O$, $M_r = 454{\cdot}50$, monoclinic, $P2_1/n$, $a = 9{\cdot}183\,(2)$, $b = 7{\cdot}3448\,(13)$, $c = 18{\cdot}272\,(3)$ Å, $\beta = 91{\cdot}640\,(15)°$, $V = 1231{\cdot}9\,(4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}23$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·710730 Å, $\mu = 0{\cdot}075$ mm^{-1}, $F(000) = 480$, $T = 183$ K, final $R = 0{\cdot}061$ for 1591 observed reflections. The structure consists of a piperazine ring in the chair conformation with the phenyl groups occupying equatorial positions. There are two propanone solvent molecules per piperazine unit. All exterior and interior bond angles of the piperazine ring are approximately tetrahedral.

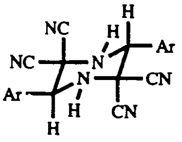
Introduction. Aminopropanedinitrile 4-methylbenzenesulfonate [aminomalononitrile *p*-toluenesulfonate (*A*)] reacts with aromatic aldehydes in methanolic sodium ethanoate to give (*E*,*E*)-4-amino-1-aryl-3-cyano-4-methoxy-2-aza-1,3-butadienes (*B*) and *trans*-2,2,5,5-tetracyano-3,6-diarylpiperazines (*C*) in good to excellent yields (Kim, 1989; Freeman & Kim, 1989, 1991). Infrared, ^{1}H NMR, ^{13}C NMR and ultraviolet spectra, and elemental analyses confirm the empirical formula of the piperazines (*C*) but cannot unambiguously assign the aryl groups to the axial or equatorial positions (diastereomers).



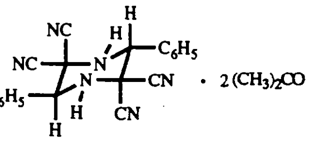
(*A*)



(*B*)



(*C*)



(*D*)

Experimental. Crystals of *trans*-2,2,5,5-tetracyano-3,6-diphenylpiperazine (*D*) were grown by slow evaporation from a solution of the compound in propanone. A colorless crystal of approximate dimensions 0·17 × 0·20 × 0·33 mm was oil mounted on a glass fiber. Data were collected on a Nicolet *P*3 diffractometer equipped with a modified LT-2 apparatus using standard techniques (Churchill, Lashewycz & Rotella, 1977). θ–2θ scans for $2\theta = 4{\cdot}0$–$50{\cdot}0°$

---

* To whom correspondence should be addressed.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement coefficients* (Å^2 × 10^4) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	4142 (3)	811 (4)	4397 (1)	293 (9)
C(2)	4733 (3)	770 (4)	5706 (1)	279 (8)
C(3)	4027 (3)	569 (4)	6420 (2)	321 (9)
C(4)	5485 (3)	2581 (4)	5704 (2)	308 (9)
C(5)	2903 (3)	778 (3)	3836 (1)	263 (8)
C(6)	3068 (3)	1695 (4)	3182 (2)	325 (9)
C(7)	1974 (3)	1675 (4)	2647 (2)	369 (10)
C(8)	685 (3)	771 (4)	2763 (2)	360 (9)
C(9)	491 (3)	−138 (4)	3417 (2)	360 (9)
C(10)	1601 (3)	−139 (4)	3951 (2)	311 (9)
N(1)	3603 (2)	632 (3)	5134 (1)	299 (7)
N(2)	3490 (3)	385 (4)	6968 (2)	553 (11)
N(3)	5999 (3)	3995 (4)	5689 (1)	431 (9)
O(1)	1500 (3)	3222 (3)	5640 (2)	761 (11)
C(11)	−312 (3)	5078 (5)	6121 (2)	580 (13)
C(12)	1206 (4)	4655 (4)	5923 (2)	451 (11)
C(13)	2330 (4)	6066 (6)	6111 (2)	690 (15)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(5)	1·510 (4)	C(1)—N(1)	1·454 (3)
C(1)—C(2′)	1·569 (4)	C(2)—C(3)	1·480 (4)
C(2)—C(4)	1·499 (4)	C(2)—N(1)	1·455 (3)
C(2)—C(1′)	1·569 (4)	C(3)—N(2)	1·137 (4)
C(4)—N(3)	1·142 (4)	C(5)—C(6)	1·384 (4)
C(5)—C(10)	1·394 (4)	C(6)—C(7)	1·382 (4)
C(7)—C(8)	1·379 (4)	C(8)—C(9)	1·385 (4)
C(9)—C(10)	1·390 (4)	O(1)—C(12)	1·206 (4)
C(11)—C(12)	1·483 (5)	C(12)—C(13)	1·496 (5)

C(5)—C(1)—N(1)	111·0 (2)	C(5)—C(1)—C(2′)	113·1 (2)
N(1)—C(1)—C(2′)	106·7 (2)	C(3)—C(2)—C(4)	107·7 (2)
C(3)—C(2)—N(1)	107·7 (2)	C(4)—C(2)—N(1)	112·2 (2)
C(3)—C(2)—C(1′)	109·8 (2)	C(4)—C(2)—C(1′)	110·6 (2)
N(1)—C(2)—C(1′)	108·7 (2)	C(2)—C(3)—N(2)	178·9 (3)
C(2)—C(4)—N(3)	176·8 (3)	C(1)—C(5)—C(6)	118·7 (2)
C(1)—C(5)—C(10)	122·6 (2)	C(6)—C(5)—C(10)	118·8 (2)
C(5)—C(6)—C(7)	120·7 (3)	C(6)—C(7)—C(8)	120·4 (3)
C(7)—C(8)—C(9)	119·8 (3)	C(8)—C(9)—C(10)	119·7 (3)
C(5)—C(10)—C(9)	120·6 (3)	C(1)—N(1)—C(2)	113·9 (2)
O(1)—C(12)—C(11)	120·7 (3)	O(1)—C(12)—C(13)	122·8 (3)
C(11)—C(12)—C(13)	116·5 (3)		

($0 \le h \le 10$, $0 \le k \le 8$, $-21 \le l \le 21$) yielded 2315 reflections which were merged to 1975 unique reflections ($R_{\text{int}} = 3{\cdot}35\%$) with $|F_o| > 0$. Standard reflections $\bar{3}10$, 020, $01\bar{4}$ showed no variation or decay during data collection. Data were corrected for Lorentz and polarization effects and for extinction $\{\chi = 0{\cdot}0011\ (6)$ where $F^* = F[1 + 0{\cdot}002\chi F^2/\sin(2\theta)]^{-1/4}\}$. The space group was determined to be $P2_1/n$ from systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. Crystallographic calculations were carried out using either our locally modified version of the *UCLA* package (Strouse, 1981) or the *SHELXTL-Plus* program set (Sheldrick, 1988). The analytical scattering factors for neutral atoms were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included (*International Tables for X-ray Crystallography*, 1974, Vol. IV, pp. 99–101, 149–150). The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0{\cdot}0003(|F_o|)^2$. The structure was solved by direct methods and refined by full-matrix least-squares techniques based on F using *SHELXTL-Plus*. All 17 symmetry-independent non-H atoms were located from the initial electron density map. The molecule lies on a center of inversion at ($\frac{1}{2}$, 0, $\frac{1}{2}$) located at the center of the ring defined by C(1), N(1), C(2), C(1′), N(1′) and C(2′). There are two propanone solvent molecules per piperazine unit. H-atom contributions were included using a riding model with d(C—H) = 0·96 Å and $U_{\text{iso}} = 0{\cdot}08$ Å^2. Refinement of positional and thermal parameters led to convergence with $R = 0{\cdot}061$, $wR = 0{\cdot}070$ and GOF = 2·36 for 155 variables refined against those 1591 data with $|F_o| > 4{\cdot}0\sigma(|F_o|)$. A final difference Fourier map showed no significant features, $\rho_{\max} = 0{\cdot}57$, $\rho_{\min} = -0{\cdot}36$ e Å^{-3}. The largest and mean Δ/σ in the final refinement cycle were 0·001 and < 0·001.* Table 1 lists atomic coordinates and thermal parameters and Table 2 bond lengths and angles.

Discussion. Although piperazine is a conformationally flexible molecule in which ring inversion and pyramidal atomic inversion at each N atom occur, most of the physical evidence indicates a preference for a chair conformation in which the N—H bonds

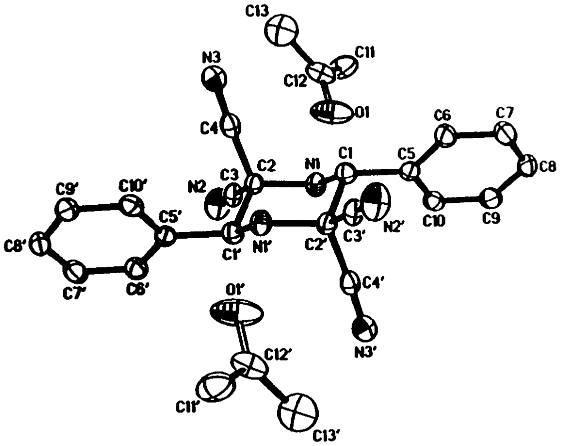


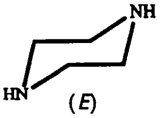
Fig. 1. *ORTEP* view of the molecular structure of *trans*-2,2,5,5-tetracyano-3,6-diphenylpiperazine–propanone (1/2) (*D*). Thermal ellipsoids are drawn at the 40% probability level. H atoms have been omitted for clarity.

---

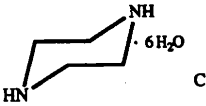
* Lists of structure factors and anisotropic displacement coefficients have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54099 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

prefer the equatorial orientation. Fig. 1 shows that the piperazine ring in *trans*-2,2,5,5-tetracyano-3,6-diphenylpiperazine–propanone (1/2) (*D*) is in the chair conformation and that the phenyl rings occupy equatorial positions. There are two propanone solvent molecules per piperazine unit and there is no hydrogen bonding between the propanone molecules. The closest distances (2·43 Å) between molecules in the unit cell are between the hydrogen on N(1) of piperazine and the oxygen O(1) of propanone. All exterior and interior bond angles of the piperazine ring system in (*D*) are approximately tetrahedral.

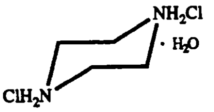
The C(1)—N(1)—C(2) bond angle of 113·9 (2)° in the highly substituted piperazine (*D*) is larger than the C—N—C bond angles observed in gaseous piperazine (*E*), 109·0 (8)° (Yokozeki & Kuchitsu, 1971), in piperazine hexahydrate (*F*), 109·3 (3)° (Schwarzenbach, 1968), in piperazine dihydrogen dichloride monohydrate (*G*), 110·9° (Rérat, 1960), in *trans*-2,5-dimethylpiperazine (*H*), 110·9 (2)° (Okamoto, Sekido, Ono, Noguchi & Hirokawa, 1982), and in *trans*-2,5-dimethylpiperazine dihydrogen dichloride (*I*), 112·4 (3)° (Bart, Bassi & Scordamaglia, 1978).



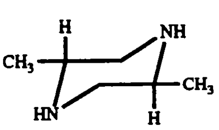
(*E*)



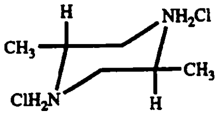
(*F*)



(*G*)



(*H*)



(*I*)

The C(1)—N(1) and C(2)—N(1) interatomic distances of 1·454 (3) and 1·455 (3) Å, respectively, in piperazine (*D*) are in the lower range of the C—N bond lengths (1·46 to 1·51 Å) of those found in other piperazine studies [(*E*) 1·467 (4), (*F*) 1·458 (4) and 1·459 (4), (*G*) 1·490 and 1·509, (*H*) 1·463 (3) and 1·465 (3), and (*I*) 1·509 (9) Å]. The C(1)—C(2′) bond lengths [1·569 (4) Å] in the piperazine ring of (*D*) are longer than the corresponding C—C bond lengths in the piperazines (*E*) [1·540 (8)], (*F*) [1·491 (5)], (*G*) (1·527), (*H*) [1·521 (3)] and (*I*) [1·534 (12) Å].

Funds for the purchase of the Nicolet *R3m/V* diffractometer system were made available from the National Science Foundation under grant CHE-85-14495, and we thank the Niels Clauson–Kaas Laboratory, Farnum, Denmark, for the generous sample of aminomalononitrile tosylate (AMNT).

References

Bart, J. C. J., Bassi, I. W. & Scordamaglia, R. (1978). *Acta Cryst.* B**34**, 2760–2764.
Churchill, M. R., Lashewycz, R. A. & Rotella, F. J. (1977). *Inorg. Chem.* **16**, 265–271.
Freeman, F. & Kim, D. S. H. L. (1989). *Synthesis*, pp. 698–699.
Freeman, F. & Kim, D. S. H. L. (1991). *J. Org. Chem.* **56**, 657–663.
Kim, D. S. H. L. (1989). MS Thesis, Univ. of California, Irvine, USA.
Okamoto, K., Sekido, K., Ono, H., Noguchi, T. & Hirokawa, S. (1982). *Bull. Chem. Soc. Jpn*, **55**, 945–946.
Rérat, C. (1960). *Acta Cryst.* **13**, 459–468.
Schwarzenbach, D. (1968). *J. Chem. Phys.* **48**, 4134–4140.
Sheldrick, G. M. (1988). *SHELXTL-Plus Structure Determination Programs.* Nicolet Instrument Corporation, Madison, Wisconsin, USA.
Strouse, C. (1981). *UCLA Crystallographic Computing Package.* Univ. of California, Los Angeles, USA.
Yokozeki, A. & Kuchitsu, K. (1971). *Bull. Chem. Soc. Jpn*, **44**, 2352–2356.

Acta Cryst. (1991). C**47**, 2124–2127

Structure of (*E*,*E*)-4-Amino-3-cyano-1-(4-hydroxyphenyl)-4-methoxy-2-aza-1,3-butadiene

By Fillmore Freeman,* Darrick S. H. L. Kim and Joseph W. Ziller

Department of Chemistry, University of California at Irvine, Irvine, California 92717, USA

(*Received* 11 *May* 1990; *accepted* 18 *March* 1991)

Abstract. (*E*,*E*)-4-Amino-1-(4-hydroxyphenyl)-4-methoxy-2-aza-1,3-butadiene-3-carbonitrile, $C_{11}H_{11}N_3O_2$, $M_r = 217·20$, monoclinic, $P2_1/n$, $a = 8·6958 (11)$, $b = 10·4009 (12)$, $c = 12·297 (3)$ Å, $\beta = 107·174 (15)°$, $V = 1062·6 (3)$ Å^3, $Z = 4$, $D_x = 1·36$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·710730 Å, $\mu = 0·090$ mm^{-1}, $F(000) =$

---

* To whom correspondence should be addressed.

0108-2701/91/102124-04$03.00