that of the N atoms surrounding each Cl⁻ ion in spermidine trihydrochloride (Giglio, Liquori, Puliti & Ripamonti, 1966*b*).

Woo, Seeman & Rich (1979) find a *gauche–trans* conformation for putrescine in the diphosphate. They point out that while in such a conformation the putrescine molecule can fit across the major groove of both A-RNA and ApU-RNA but cannot bridge the DNA helix, in the all-*trans* conformation it can bridge the DNA double helix as well as RNA helices, forming two hydrogen bonds in each case. Indeed, we do find an all-*trans* conformation for putrescine in PDH. In this context, the distances between the eight Cl⁻ ions surrounding each putrescine molecule may be of interest and these are listed in Table 4.

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References

ASHIDA, T. & HIROKAWA, S. (1963*a*). *Bull. Chem. Soc. Jpn*, **36**, 704–707.

ASHIDA, T. & HIROKAWA, S. (1963*b*). *Bull. Chem. Soc. Jpn*, **36**, 1086–1091.

BINNIE, W. P. & ROBERTSON, J. M. (1949). *Acta Cryst.* **2**, 180–188.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

DONOHUE, J. (1952). *J. Phys. Chem.* **56**, 502–510.

GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). Program *UCLALS* 1. Univ. of California, USA.

GIGLIO, E., LIQUORI, A. M., PULITI, R. & RIPAMONTI, A. (1966*a*). *Acta Cryst.* **20**, 652–659.

GIGLIO, E., LIQUORI, A. M., PULITI, R. & RIPAMONTI, A. (1966*b*). *Acta Cryst.* **20**, 683–688.

HIROKAWA, S., OHASHI, T. & NITTA, I. (1954). *Acta Cryst.* **7**, 87–91.

HUGHES, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.

HUSE, Y. & IITAKA, Y. (1969). *Acta Cryst.* **B25**, 498–509.

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

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1966). *Acta Cryst.* **A24**, 351–359.

SHIONO, R. (1968). A block-diagonal least-squares program for the IBM-1130 computer. Department of Crystallography, Univ. of Pittsburgh, USA.

SØTOFTE, I. (1976). *Acta Chem. Scand. Ser. A*, **30**, 309–311.

TAKUSAGAWA, F. & KOETZLE, T. F. (1978). *Acta Cryst.* **B34**, 1910–1915.

TAKUSAGAWA, F. & KOETZLE, T. F. (1979). *Acta Cryst.* **B35**, 867–877.

WOO, N. H., SEEMAN, N. C. & RICH, A. (1979). *Biopolymers*, **18**, 539–552.

WRIGHT, D. A. & MARSH, R. E. (1962). *Acta Cryst.* **15**, 54–64.

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Bis(4-nitrophenyl) Ketone

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Abstract. $C_{13}H_8N_2O_5$, triclinic, $P\bar{1}$, $a = 7\cdot323$ (2), $b = 12\cdot634$ (4), $c = 13\cdot301$ (3) Å, $\alpha = 89\cdot37$ (2), $\beta = 86\cdot75$ (2), $\gamma = 87\cdot09$ (3)°, $Z = 4$, $d_c = 1\cdot463$, $d_m = 1\cdot46$ Mg m^{-3}. $R = 0\cdot037$ for 1385 observations measured by diffractometer. The two independent molecules of the asymmetric unit exist in approximate C_2 conformations, with the aromatic rings tipped an average of 28° out of the plane of the ketone unit. The nitro substituents are essentially coplanar with the aromatic rings. The formula given above has been definitively determined by crystallographic tests as well as other physical and spectral techniques.

Introduction. The recent discovery of a facile means of decarbonylation (Newkome & Taylor, 1979) led us to attempt the synthesis of cyclobuta[1,2-*b*:4,3-*b*′]dipyridine (I) from 1,8-diazafluorenone (II) by treatment with sodium hydride in xylene.

(II) (I)

Rather than the anticipated compound, chemical decarbonylation produced predominantly an uncharacterized black material. Also isolated from the reaction mixture was a minute quantity of pale-yellow needles

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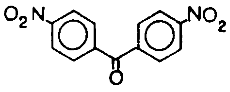
(m.p. 472–473 K). Since standard spectral data (NMR, IR, MS) afforded little assistance in the identification of this crystalline substance, X-ray diffraction techniques were employed to ascertain the structure of what proved to be bis(4-nitrophenyl) ketone.



Intensity data were obtained from a crystal of dimensions 0·68 x 0·42 x 0·28 mm sealed in a thin-walled glass capillary and mounted in random orientation on an Enraf–Nonius CAD-4 automatic diffractometer. One hemisphere of data with $2° \leq 2\theta \leq 50°$ was collected, using Mo $K\alpha$ radiation (λ = 0·71073 Å). The ω–2θ scans were made at variable speeds, adjusted to yield a net intensity of approximately 4000 counts. Weak reflections measuring less than 30 net counts in a 20° min^{-1} prescan were flagged as unobserved by the diffractometer. No appreciable decrease in the intensities of standard reflections was noted. A total of 2667 reflections were measured in this manner, of which 1385 were considered significantly intense to be used in further calculations. Data were corrected for background, Lorentz and polarization effects, but not for absorption (μ = 0·104 mm^{-1}), and were placed on an absolute scale by statistical methods.

Attempts to solve the structure by direct methods using only observed reflections invariably failed. It was believed that this failure was primarily due to the large number of unobserved reflections, which were not carefully measured by the diffractometer and thus not included in the original data set. Their absence prevented proper normalization of the structure factors, and this, rather than the complexity of the structure, appeared to prevent structure solution. This difficulty was circumvented by temporarily assigning random values to F_o of the unobserved reflections, such that the distribution of the assigned values was that statistically expected based upon the distribution of the observed structure factors (Vicković & Viterbo, 1979). A set of 758 weak reflections was thus added to the dataset for the purpose of direct methods, and later removed. Scale and temperature factors derived by the method of Wilson (1942) were changed considerably by this insertion, having values B = 1·83 Å^2, SCALE = 1·97 before and B = 2·78 Å^2, SCALE = 2·39 afterwards. With the revised dataset, the program *MULTAN* 80 (Germain, Main & Woolfson, 1980) yielded the correct positions of all nonhydrogen atoms on the first E map.

Refinement was based on F_o with unit weights, anisotropic temperature factors for the nonhydrogen atoms, and H atoms placed in calculated positions with a common isotropic temperature factor. Convergence was achieved with R = 0·037, and a difference Fourier map yielded no residuals greater than ±0·12 e Å^{-3}.*

Discussion. Refined coordinates and equivalent isotropic temperature factors (Hamilton, 1959) for nonhydrogen atoms are given in Table 1. Fig. 1 illustrates average distances and angles involving nonhydrogen atoms. The averages are taken over the independent fragment in ideal molecular symmetry C_2, as well as over the two independent molecules within the asymmetric unit. Agreement between the four averaged values is generally quite good; a few

Table 1. *Coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\times 10^3$)

	x	y	z	U_{eq} (Å^2)
C(1)	7459 (8)	8191 (5)	5206 (5)	60 (4)
O(1)	6838 (6)	8514 (3)	6023 (3)	80 (3)
C(2)	7494 (7)	7015 (4)	5008 (4)	54 (3)
C(3)	7804 (8)	6324 (5)	5800 (4)	68 (4)
C(4)	7756 (8)	5246 (5)	5664(5)	70 (4)
C(5)	7373 (8)	4887 (4)	4739 (5)	62 (3)
C(6)	7033 (4)	5539 (5)	3946 (5)	67 (4)
C(7)	7120 (8)	6617 (4)	4075 (4)	64 (3)
N(1)	7262 (8)	3721 (4)	4603 (6)	81 (4)
O(2)	7608 (7)	3143 (4)	5299 (4)	117 (3)
O(3)	6808 (8)	3425 (4)	3791 (5)	113 (4)
C(2′)	8196 (7)	8937 (4)	4436 (4)	52 (3)
C(3′)	7650 (7)	10007 (4)	4534 (4)	58 (3)
C(4′)	8346 (8)	10749 (4)	3873 (4)	59 (3)
C(5′)	9582 (8)	10401 (4)	3114 (4)	57 (3)
C(6′)	10152 (8)	9360 (5)	2997 (4)	59 (3)
C(7′)	9462 (8)	8628 (4)	3663 (4)	58 (3)
N(1′)	10317 (8)	11183 (5)	2391 (4)	73 (4)
O(2′)	9956 (6)	12127 (4)	2555 (3)	93 (3)
O(3′)	11237 (6)	10870 (4)	1647 (3)	90 (3)
C(1*A*)	6748 (9)	2984 (5)	800 (4)	62 (4)
O(1*A*)	8190 (6)	3266 (3)	414 (3)	83 (3)
C(2*A*)	6488 (8)	1824 (4)	1002 (4)	56 (3)
C(3*A*)	7370 (8)	1087 (5)	342 (4)	67 (4)
C(4*A*)	7216 (9)	21 (5)	527 (5)	72 (4)
C(5*A*)	6233 (9)	−281 (4)	1372 (5)	63 (3)
C(6*A*)	5361 (8)	418 (5)	2052 (4)	64 (4)
C(7*A*)	5496 (8)	1493 (4)	1845 (4)	59 (3)
N(1*A*)	6036 (9)	−1438 (5)	1593 (5)	86 (4)
O(2*A*)	6742 (8)	−2042 (4)	977 (5)	135 (3)
O(3*A*)	5211 (8)	−1693 (4)	2363 (4)	109 (4)
C(2*A*′)	5226 (9)	3785 (4)	1079 (4)	55 (3)
C(3*A*′)	5718 (8)	4807 (5)	1277 (4)	60 (3)
C(4*A*′)	4381 (9)	5589 (5)	1508 (4)	64 (4)
C(5*A*′)	2576 (9)	5330 (5)	1519 (4)	61 (3)
C(6*A*′)	2031 (8)	4329 (4)	1303 (4)	63 (3)
C(7*A*′)	3391 (9)	3552 (4)	1090 (4)	62 (3)
N(1*A*′)	1116 (9)	6167 (5)	1790 (4)	78 (4)
O(2*A*′)	1626 (7)	7052 (4)	1904 (4)	114 (4)
O(3*A*′)	−435 (8)	5931 (4)	1862 (5)	125 (4)

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* Lists of structure factors, anisotropic thermal parameters and assigned H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35409 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

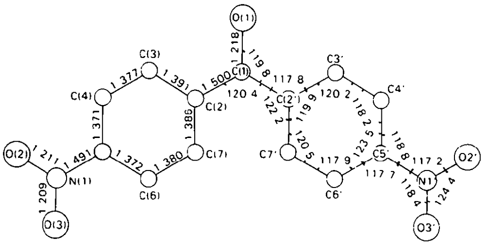

Fig. 1. Average distances (Å) and angles (°) in bis(4-nitrophenyl) ketone. Standard deviations in individual values are 0·006–0·008 Å, and 0·3–0·6 °.

differences of marginal significance are noted. No unusual distances or angles are observed. Except for a few small differences in the dimensions of the aromatic rings attributed to the effects of nitro substitution, distances and angles agree well with those in benzophenone (Fleischer, Sung & Hawkinson, 1968).

The conformation of the molecule deviates considerably from both possible structures of ideal symmetry C_{2v}. Important torsion angles are listed in Table 2. Those about the four bonds chemically equivalent to C(1)—C(2) indicate closer approximation to C_2 symmetry. The average of these torsion angles, −28°, is in exact agreement with the average found in benzophenone (Fleischer, Sung & Hawkinson, 1968). Torsion angles about the C—N bonds are all less than 10°, indicating that the nitro substituents are nearly coplanar with the aromatic rings.

Table 2. *Important torsion angles*

O(1)–C(1)–C(2)–C(3)	−35·0 (8)°
O(1)–C(1)–C(2′)–C(3′)	−20·2 (8)
C(6)–C(5)–N(1)–O(3)	−2·6 (7)
C(6′)–C(5′)–N(1′)–O(3′)	8·8 (7)
O(1*A*)–C(1*A*)–C(2*A*)–C(3*A*)	−33·0 (8)
O(1*A*)–C(1*A*)–C(2*A*′)–C(3*A*′)	−25·4 (8)
C(6*A*)–C(5*A*)–N(1*A*)–O(3*A*)	−3·8 (7)
C(6*A*′)–C(5*A*′)–N(1*A*′)–O(3*A*′)	4·1 (7)

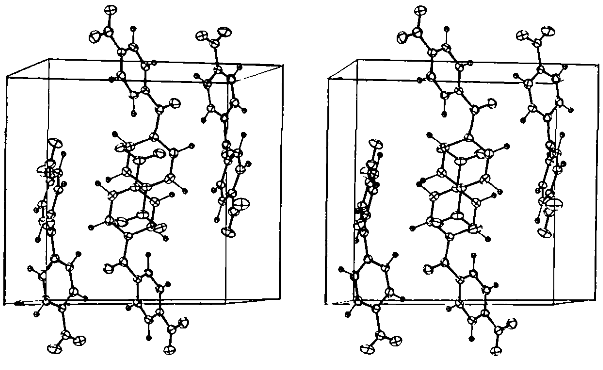

Fig. 2. A stereoview of the crystal packing (Johnson, 1965). Thermal ellipsoids are drawn at the 30% probability level, and H atoms are represented by spheres of arbitrary size.

Packing of the molecules in the crystal structure is illustrated in Fig. 2; normal parallel stacking of the aromatic groups is evident. No unusually close intermolecular contacts exist.

At the beginning of this investigation the identity of the molecule was unknown. Crystallographic evidence was considered necessary to distinguish between alternative formulations. Particularly, bis(4-carboxyphenyl) ketone was considered a likely possibility, as this compound has been shown to be an impurity which arises from the conversion of *p*-xylene to terephthalic acid (Kaminskii, Grudtsyn, Agapova & Gitis, 1972), and is present in trace amounts in the stabilizer mixture of reagent xylene and most common halogenated solvents. Although the dicarboxylic acid model could be refined to an *R* value of 0·046, it has been ruled out on purely crystallographic grounds as well as other physical tests and spectral evidence. First, the necessary acid H atoms could not be located (maximum residual 0·16 e Å^{-3}), even though the phenyl H atoms were extremely clear from difference maps. The central C atoms of the carboxyl groups refined to have temperature factors which were the smallest of the structure, and bonds to these atoms were shorter than expected for even C=O double bonds. The molecular packing was also not indicative of a carboxylic acid, lacking significant hydrogen bonding. Refinement as the dinitro compound is much more satisfactory, resulting in a lower *R* factor by about 1%, reasonable temperature factors for the N atoms, reasonable distances, and understandable packing. The improvement in the *R* factor is significant at better than the 99% probability level (Hamilton, 1965).

Other evidence for the dinitro formulation includes the presence of a peak with $M_r = 272$ and a reasonable fragmentation pattern in the mass spectrum, and essentially identical proton NMR ($CDCl_3$) δ 7·99 (*d*, 2,6-Ph-H, 4H), δ 8·39 p.p.m. (*d*, 3,5-Ph-H, 4H) and a TLC R_f value identical to that of an authentic sample of bis(4-nitrophenyl) ketone.

While the identity of the title compound is unequivocal, its origin remains a mystery.

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References

FLEISCHER, E. B., SUNG, N. & HAWKINSON, S. (1968). *J. Phys. Chem.* **72**, 4311–4312.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1980). Personal communication.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

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

Kaminskii, A. Ya., Grudtsyn, Yu. D., Agapova, S. A. & Gitis, S. S. (1972). *Tr. Vses. Nauchno-Issled. Proektn. Inst. Monomerov*, **3**, 119–125.

Newkome, G. R. & Taylor, H. C. R. (1979). *J. Org. Chem.* **46**, 1362–1363.

Vicković, I. & Viterbo, D. (1979). *Acta Cryst.* A**35**, 500–501.

Wilson, A. J. C. (1942). *Nature* (*London*), **150**, 151–152.

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Refinement of Di-*para*-anthracene*

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Abstract. $(C_{14}H_{10})_2$, orthorhombic, *Pbca*, a = 12·085 (4), b = 18·853 (7), c = 8·139 (3) Å, Z = 4, D_x = 1·28 Mg m^{-3}; R = 0·040 and R_w = 0·042 for 1019 observed intensities. The crystal structure has been refined by using single-crystal X-ray diffraction data. The molecule consists of two bent anthracenes bridged by a pair of long C—C bonds (1·624 Å), and possesses pseudo *mmm* symmetry.

Introduction. The crystal structure of di-*para*-anthracene has been determined by Ehrenberg (1966). The data used in the study were a limited number of reflection intensities measured by visual comparison of Weissenberg photographs from two different crystals. The present study was intended to supplement Ehrenberg's work by using accurate single-crystal X-ray diffraction data.

A small crystal, about 0·2 mm diameter and 0·3 mm long, was grown from an acetone solution of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine mixed with anthracene by photo-dimerization under ultraviolet light. Two equivalent sets of reflections within the limiting sphere of 0·65 Å^{-1} in sin θ/λ were measured with Mo $K\alpha$ radiation, with an ω–2θ continuous scan and a scan speed of 1° min^{-1}. The intensities of three standard reflections (600, 010, and 002), measured periodically after every fifty reflection measurements, decreased gradually to 60% of their original intensities at the end. Therefore, the observed data were corrected for the average decrease obtained from these standard reflections. The agreement between the equivalent reflections was satisfactory, with a conventional R = 0·020. 1609 independent reflection data were collected, of which only 1019 had observable intensities according to the criterion $I \geq 3\sigma(I)$, where $\sigma = (I + B)^{1/2}$, I and B being the peak and background intensities respectively. The structure was solved by a direct method using XRAY 76 (Stewart, 1976). H atoms were located by a difference Fourier synthesis.

Table 1. *Positional parameters of di-para-anthracene*

For C atoms B is the equivalent value of the anisotropic temperature factor.

	x	y	z	B (Å^2)
C(1)	0·4062 (2)	0·1285 (1)	0·2313 (3)	4·17
C(2)	0·3104 (2)	0·1669 (1)	0·1945 (3)	4·78
C(3)	0·2363 (2)	0·1404 (1)	0·0812 (3)	4·80
C(4)	0·2554 (2)	0·0755 (1)	0·0064 (3)	4·16
C(5)	0·3903 (2)	−0·1538 (1)	0·1043 (3)	4·25
C(6)	0·4376 (2)	−0·1975 (1)	0·2223 (3)	4·87
C(7)	0·5153 (2)	−0·1710 (1)	0·3302 (3)	4·82
C(8)	0·5455 (2)	−0·0999 (1)	0·3216 (3)	4·17
C(9)	0·5309 (2)	0·0214 (1)	0·1848 (2)	3·53
C(10)	0·3792 (2)	−0·0328 (1)	−0·0390 (3)	3·68
C(11)	0·4222 (2)	−0·0834 (1)	0·0918 (3)	3·53
C(12)	0·4997 (2)	−0·0560 (1)	0·2034 (2)	3·46
C(13)	0·4264 (2)	0·0640 (1)	0·1557 (2)	3·51
C(14)	0·3499 (2)	0·0366 (1)	0·0432 (2)	3·57
H(1)	0·463 (2)	0·150 (1)	0·305 (2)	1·9 (5)
H(2)	0·293 (2)	0·213 (1)	0·248 (3)	2·5 (5)
H(3)	0·167 (2)	0·167 (1)	0·058 (3)	4·1 (7)
H(4)	0·203 (2)	0·056 (1)	−0·071 (3)	2·8 (6)
H(5)	0·334 (2)	−0·171 (1)	0·026 (3)	2·4 (5)
H(6)	0·417 (2)	−0·249 (1)	0·232 (3)	3·2 (6)
H(7)	0·555 (2)	−0·203 (1)	0·415 (3)	3·2 (6)
H(8)	0·606 (2)	−0·080 (1)	0·395 (2)	1·3 (5)
H(9)	0·567 (2)	0·038 (1)	0·290 (2)	0·9 (4)
H(10)	0·314 (2)	−0·053 (1)	−0·090 (2)	0·8 (4)

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* Bi(9,10-dihydro-9,10-anthracenediyl).

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