A Model for the Attack of a Nucleophile on a Nitrile Group: The X-Ray Crystal Structure of 2,2′-Bipyridine-3,3′-dicarbonitrile

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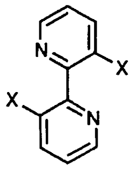
From analysis of the geometry of the attractive intramolecular interactions between the pyridine N atoms and the nitrile C atoms in title compound **2** it is proposed that the most favoured direction of approach of a nucleophile to an sp $C(\equiv N)$ makes an angle of at least 108° to the triple bond.

Attractive interactions between functional groups have only been measured in a few cases,[1] yet they are likely to be common in sterically congested compounds and may play a significant role in molecular recognition processes. The 3,3′-disubstituted 2,2′-bipyridine system **1** provides a potentially very useful framework for investigating the interaction between a nucleophilic centre, a pyridine N atom and an electrophilic substituent placed on the other ring. These two groups lie closest together when the bipyridine is in a *trans*



1
2 X = CN

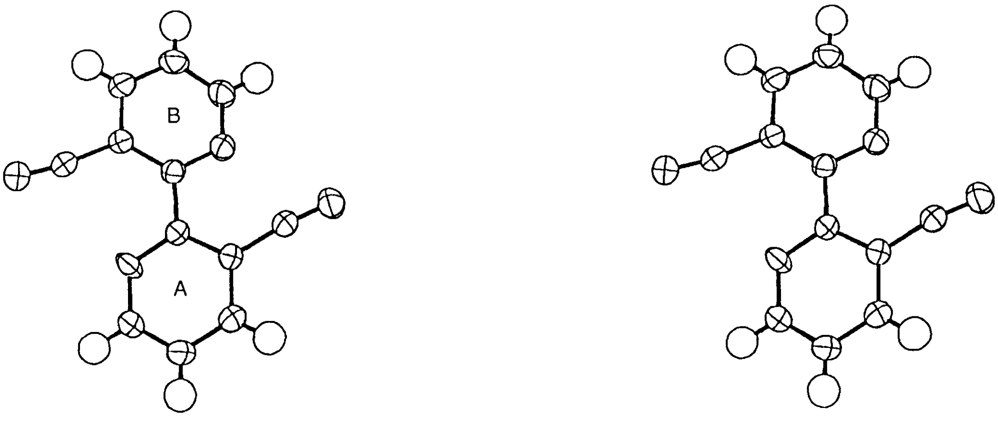


Fig. 1 Stereoview of **2** (ORTEP)

coplanar conformation, yet their mutual orientations can be considerably modified by small rotations about the inter-ring bond. In appropriate cases such an interaction represents an early stage in the corresponding chemical reaction[2] and can provide important information on the stereoelectronic control of this process. We now report the first X-ray crystal structure of this type of molecule, the 3,3′-dicarbonitrile **2**.

This substance was prepared by Ullmann coupling of 2-bromopyridine-3-carbonitrile[3] with copper bronze in dimethylformamide at 150 °C. Details of the isolation and purification to give colourless crystals (m.p. 247.5–248 °C, 39%) are given below.[†] A sample for X-ray diffraction was grown by vacuum sublimation.[‡]

The molecular structure of **2** is illustrated in Fig. 1 and important features of its geometry are given in Fig. 2. The two rings are labelled A and B. The angle between the best planes of the pyridine rings is 23.6° and there are short attractive interactions between each pyridine N atom and adjacent nitrile C atom. The separations of these atoms (2.69 and 2.74 Å) are considerably shorter than the sum of corresponding van der Waals radii (3.2 Å). Both C–C≡N groups are bent by *ca.* 8.5° from linearity such that the central sp C atom deviates from the vector through its neighbours towards the adjacent pyridine N atom. The N(pyridine) · · · C≡N angles are both very close to 108° and we believe represent the most favourable mutual orientations available to these groups in this molecule; if the pyridine rings were coplanar (and the π-overlap between rings at a maximum) the N · · · C distances would be little changed but the angle of approach of the pyridine N atom to the triple bond would be decreased to *ca.* 99°, while if the angle between the pyridine rings were increased the N · · · C distance would also increase. This result is in line with the proposal that the energetically most favourable approach of a nucleophile to a C,C or C,N triple bond makes an obtuse angle to the triple bond rather than an acute one[6] and indicates that for a nitrile group this angle is at least 108°.

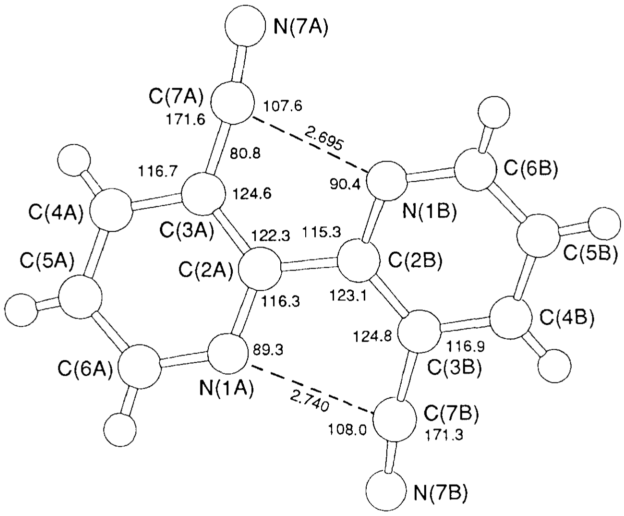


Fig. 2 Selected molecular geometry for **2**. Esds on interatomic distances 0.002 Å, on angles 0.1°. Deviations (Å × 10^3) from best plane of (*i*) ring (A): N(1A) 1, C(2A) −1, C(3A) 1, C(4A) −1, C(5A) 1, C(6A) −1, C(7A) −48, N(7A) −120, N(1B) 474, C(7B) −1021, N(7B) −1476; from (*ii*) ring B: N(1B) 6, C(2B) −8, C(3B) 3, C(4B) 4, C(5B) −6, C(6B) 2, C(7B) −18, N(7B) −40, N(1A) 419, C(7A) −1093, N(7A) −1590.

It is particularly noteworthy that these angles of approach (107.6 and 108.0°) have been optimised rather than the N(1A) · · · C(7B) and N(1B) · · · C(7A) separations which differ by 0.05 Å. This is achieved in two ways. There are very similar 'in plane' distortions of the *exo* angles at C(2A) and C(3A), and C(2B) and C(3B) such that the nitrile groups are bent away from the 'attacking' pyridine N atoms, which are themselves bent towards the 'attacked' nitriles (Fig. 2). Distortions in the opposite sense would decrease this angle of attack. In contrast the 'out of plane' distortions from each ring are not equivalent. The B pyridine ring is slightly folded about the C(2B) · · · C(5B) vector while the A ring appears to be almost completely planar. This contributes to the larger displacement of the A nitrile from its pyridine ring's best plane. There are no short intermolecular interactions.

[†] A brown solid was isolated by vacuum filtration of the reaction mixture, washed with CH_2Cl_2, dried and vacuum sublimed (185–220 °C/0.05 mmHg) to give **2**. A further small quantity of material was obtained by similar treatment of the evaporated filtrate. Purification by a second vacuum sublimation and two recrystallisations (propan-1-ol) yielded analytically pure material. Spectral data: ^1H NMR (δ/ppm $CDCl_3$): 4-H: 8.22 (dd), 5-H: 7.58 (dd), 6-H: 8.97 (dd); $J_{4,5}$ 8.0, $J_{4,6}$ 1.7, $J_{5,6}$ 4.8 Hz; ^{13}C NMR (δ/ppm $CDCl_3$): 2-C: 156.1, 3-C: 109.3, 4-C: 142.4, 5-C: 124.1, 6-C: 151.7, C≡N: 116.4; IR ν/cm^{-1} (vacuum sublimed thin film): 2225s, 1576m, 1552m, 1418s, 1040m, 813s, 738s; mass spectrum *m/z* (I%) 206 (100, M$^+$), 180(20), 103(28), 76(38), 50(18).

[‡] *Crystal data*: $C_{12}H_6N_4$, M_r = 206.2, a = 3.819(3), b = 10.139(3), c = 12.780(3) Å, α = 99.14(2), β = 91.03(4), γ = 98.39(4)°, V = 482.9 Å^3, Z = 2, triclinic, space group $P\bar{1}$, D_c = 1.42 g cm^{-3}, Mo-Kα radiation, Enraf-Nonius CAD-4 diffractometer, μ = 0.53 cm^{-1}, 1591 reflections with $I > 3\sigma(I)$, max. $(\sin\theta)/\lambda$ = 0.62 Å^{-1}, $F(000)$ = 212.0, structure solved by SHELXS-86[4] and refined with SHELX 76[5] with weights $w = [\sigma(F)^2 + 0.0003F^2]^{-1}$, final R = 0.040, R_w = 0.042. Atomic coordinates, bond lengths and angles, and thermal parameters for **2** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The stabilisation of the *trans* conformation of **2** affects the chemistry of this potential ligand. No complexes of the type $[M(CO)_4(ligand)]$ could be isolated, in contrast to other 2,2′-bipyridinedicarbonitriles[7] and to other 3,3′-X_2-2,2′-bipyridines (X = Me, CO_2Me).

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