trans Deformation of a Carbon–Carbon Triple Bond in Response to Incipient Nucleophilic Attack: the X-Ray Crystal Structure of Ethyl 3-(2-Nitrophenyl)propynoate at 150 K

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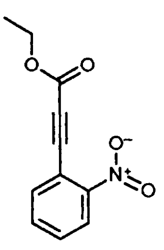
In the title compound **1** the electron-deficient alkyne bond shows a pronounced *trans* distortion in response to an adjacent electron rich nitro O atom, suggesting that the more favourable reaction coordinate for addition of nucleophiles to activated alkynes involves *trans* rather than *cis* addition.

Electron-deficient alkynes are well known to undergo addition reactions with nucleophiles such as amines, alcohols and thiols.[1–5] Experimental evidence suggests that both *cis* and *trans* additions are energetically accessible. For example, amines add to dimethyl but-2-yn-1,4-dioate predominantly by *trans* addition in methanol, but by *cis* addition in aprotic solvents[2] (though isomerisation of the initial product can complicate the situation[3]). In support of this, *ab initio* calculations by Houk *et al.*[6] for addition of ammonia to propynenitrile have indicated that the transition states for *cis*



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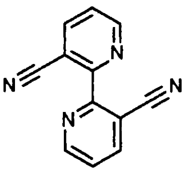

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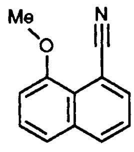

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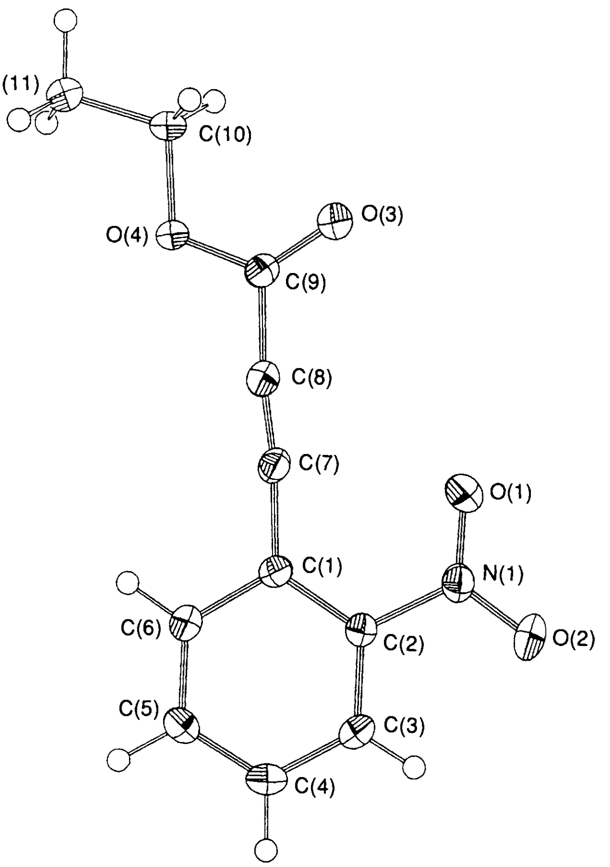

Fig. 1 Molecular structure of **1** at 150 K with anisotropic displacement parameters drawn at the 50% probability level[21]

and *trans* addition are of similar energy, with the latter slightly more stable (by 8.4 kJ mol^{-1}). To investigate this matter further we have measured the X-ray crystal structure of the 2-nitrophenylalkyne **1**† in which a nitro O atom lies adjacent to a C–C triple bond which is activated by a carboxylic ester group to nucleophilic attack. Although the nitro group may not be an obvious nucleophile, the O atoms act as very good probes for investigating the structural effects of the approach of an electron-rich centre to an electrophilic site, as has been observed in the 8-nitronaphthalene-1-diazonium cation,[7] 1,8-dinitronaphthalene[8] and 3,3′-dinitro-2,2′-bipyridine.[9] Attractive interactions between nucleophilic groups and nitrile C atoms have been observed in **2**[10] and **3**,[11] however, these structures provide no information about electronic changes at the terminal sp atom.

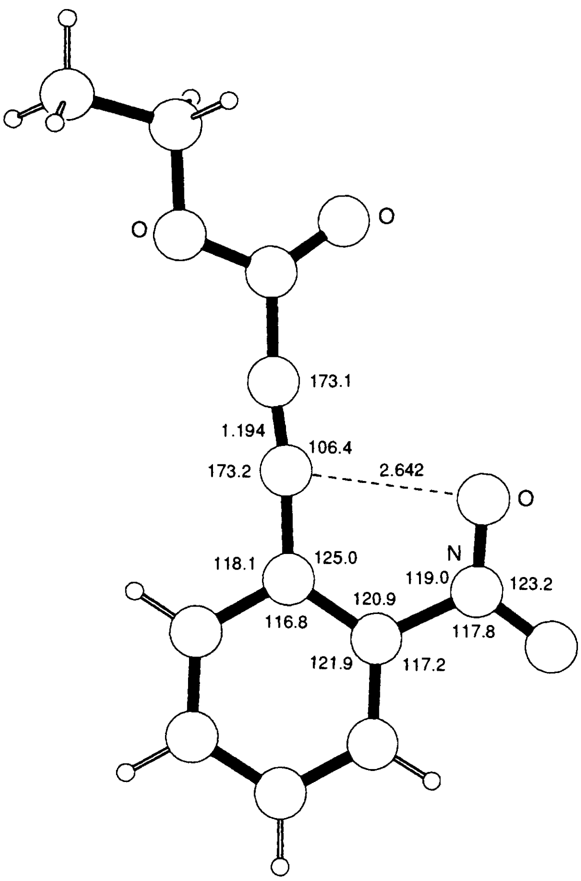

Fig. 2 Selected molecular geometry[21] for **1**. ESDs on interatomic distances 0.002 Å; on angles 0.1–0.2°. Deviations (Å × 10^3) from best plane through benzene ring: O(1) − 193, O(2) 45, N(1) − 52, C(1) 11, C(2) − 9, C(3) − 1, C(4) 10, C(5) − 7, C(6) − 2, C(7) 85, C(8) 176.

The molecular structure of **1**‡ is nearly planar (Fig. 1), the nitro group lying at only 6.7° to the best plane through the aromatic ring. There is an attractive interaction between the nitro O(1) atom and the sp C(7) atom. Details of the relevant molecular geometry are given in Fig. 2. The separation of these two atoms [2.642(2) Å] is more than 0.4 Å within the sum of the appropriate van der Waals radii. The triple bond is distorted in a *trans* mode with bonding geometries at both sp C atoms deviating by almost 7° from linearity and a C(1)–C(7)–C(8)–C(9) torsion angle of 177°. Furthermore, C(7) deviates from the C(1)···C(8) vector directly towards O(1).§ Thus the line of approach of O(1) to C(7), and the axis of the orbital of the developing carbanion at C(8) are in an antiperiplanar arrangement. The incipient carbanionic centre cannot be stabilised by the π-system of the carboxylic ester group. In this case the orientation of the ester group may be dictated by the

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† Compound **1** was prepared by conversion of *E*-3-(2-nitrophenyl)-propenoic acid into 2-nitrophenylpropynoic acid,[12] esterification with ethanol and sulfuric acid and chromatographic purification. Block-shaped crystals were grown by slow evaporation of a diethyl ether–hexane solution; ^{1}H NMR (270 MHz CDCl$_3$): δ 8.16 (dd, 3-H), 7.71 (4-,5-,6-H, m), 4.33 (q, CH$_2$), 1.37 (t, CH$_3$, $J_{3,4}$ 8.0, $J_{3,5}$ 1.4 Hz); ^{13}C NMR (67.8 MHz δ CDCl$_3$): 115.5, 1-C, 149.9, 2-C, 125.0 3-C, 131.0 4-C, 135.8 5-C, 133.3 6-C, 86.8 7-C, 80.4 8-C, 153.4 9-C, 62.5 10-C, 14.0 11-C; ν/cm^{-1} (Nujol) 2231m, 2212m, 1700s, 1520s, 1190s; *m*/*z* (I%) CI 237 (100, M + NH$_4^+$), 220 (18, M + 1$^+$), 206(25), 192(12), 147(12).

‡ *Crystal data*: C$_{11}$H$_9$NO$_4$, M_r = 219.2, m.p. 60–62 °C, a = 7.299(1), b = 19.028(3), c = 8.103(1) Å, β = 115.21(1)°, V = 1018.2 Å^3, Z = 4, monoclinic, space group $P2_1/c$, D_c = 1.43 g cm^{-3}, Mo-Kα radiation, DELFT-Instruments FAST TV area detector diffractometer, SERC Crystallography Service, University of Wales, Cardiff, data collection routines as published,[13] μ = 1.0 cm^{-1}, 1661 reflections with $I > 3\sigma(I)$, max (sinθ)/λ = 0.70 Å^{-1}, $F(000)$ = 456.0, structure solved by SHELXS-86[14] and refined with SHELX-76[15] with weights $w = [\sigma(F)^2 + 0.00001F^2]^{-1}$, final R = 0.041, R_w = 0.044. Fractional atomic coordinates, bond lengths and angles, and anisotropic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The C(7) atom lies almost exactly in the plane defined by its two bonded neighbours [C(1) and C(8)] and the O(1) atom (deviation from plane: 0.009 Å).

needs of efficient crystal packing. For a bimolecular reaction between a nucleophile and a propynoic ester, the nucleophile can attack in such an orientation that the ensuing carbanion is stabilised as an ester enolate. [The only short intermolecular contact in the crystal structure of **1** is between O(2) and the methylene hydrogen atom H(101, $2 - x, -y, 2 - z$) (2.50 Å).]

These results are in accord with Houk's prediction that the transition state with a *trans* distortion is more stable than the transition state with a *cis* distortion. However, our results only pertain to an early stage of the reaction coordinate (O···C 2.64 Å) whereas Houk's calculations refer to the transition state for the (gas phase) addition of ammonia to propynenitrile for which the $(H_3)N \cdots C(sp)$ distance was calculated to be 1.74 Å. Among the 300 alkynes in the Cambridge Structural Database such prominent *trans* distortions are very rare indeed. In contrast, quite large *cis* distortions (>20°) are observed in certain cyclic alkynes.[16]

The nitro and alkyne groups in **1** are splayed slightly in the plane of the benzene ring so that the second nitro O atom makes a short contact to the *ortho* H atom [2.36(2) Å]. In contrast, *o*-nitrophenyl compounds usually relieve inter-substituent steric interactions by rotation of the nitro group out of the benzene plane as in *E*-3-(2,4-dinitrophenyl)propenoic acid.[17] The observed conformation for **1** must be strongly influenced by the attractive nature of the O(1)···C(7) interaction. The line of approach of the O atom to C(7) lies at 106.4(2)° to the axis of the triple bond. The most energetically favourable direction of attack for nucleophiles on an alkyne bond has been a matter of some debate; both an acute angle (*ca.* 60°) and an obtuse angle (*ca.* 120°) have been proposed.[18–20]

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