Attractive Interactions Between an Alkyne Group and Two Carbonyl Oxygen Atoms: the Crystal and Molecular Structure of 2,2′-Ethynylenedibenzoic Acid at 150 K

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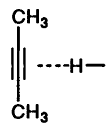
The X-ray crystal structure of **8** shows two attractive intramolecular interactions between sp carbon atoms and adjacent carbonyl oxygen atoms, leading to a twisting of the triple bond equivalent to an orthogonal combination of *cis* and *trans* bends; the two carboxylic acid groups lie to the same side of the triple bond to avoid unfavourable contacts between carbonyl oxygen atoms and incipient carbanionic centres.

Alkynes can form addition products with electrophilic or nucleophilic reagents depending on the electronic effects of the groups attached to the termini of the triple bond. Thus, the electron-rich alkyne, hex-3-yne, reacts with bromine to give (*E*)-3,4-dibromohex-3-ene,[1] while the electron-poor alkyne dimethyl but-2-ynedioate reacts with amines and thioureas to form enamines and thiazolidinones.[2] A parallel situation could be anticipated for inter- and intra-molecular contacts to alkynes. Thus, it has been noted that the π-electron density of electron-rich alkynes can form hydrogen bonds as in **1**[3] and **2**,[4] while electron-poor alkynes could be expected to form attractive interactions with electron-rich atoms. Indeed, we reported a good example of the latter recently in the 2-nitrophenylpropynoate **3**[5] in which a nitro oxygen atom makes a close contact with an sp carbon atom and induces a *trans* bend in the alkyne [C–C≡C: 173.2(1)°]. The O ··· C distance [2.642(2) Å] is *ca.* 0.5 Å within the sum of the corresponding traditional van der Waals radii.[6] This interaction may be viewed as representing an early stage in the nucleophilic attack on an electron-deficient alkyne and the geometry of the alkyne's distortion is in accord with theoretical predictions.[7] Examples of close contacts to more electrophilic triple bonds have been interpreted in a similar way, for example, from an oxygen atom or a sulfur atom to a diazonium group in **4** or **5**,[8] and from pyridine nitrogen atoms to nitrile groups in **6**.[9] We now report studies on an alkyne **8** which, unlike **3**, can react with an adjacent electron-rich atom.



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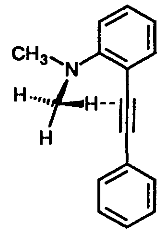

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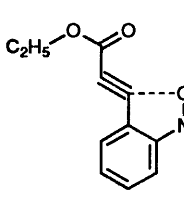

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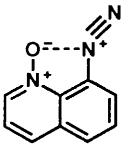

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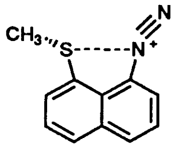

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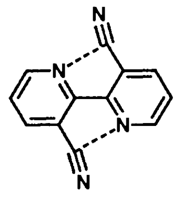

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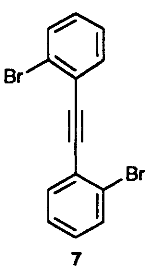
The alkyne **8** undergoes intramolecular addition of a carboxylic acid to the triple bond very readily to give lactone **9**.[10] Indeed, recrystallisation of **8** from most solvents is sufficient to effect the reaction! Studies of the pH dependence of the reaction rate have shown that the reaction proceeds by addition of a carboxylate ion to the triple bond, yet the fast rate of reaction is due to the presence of the second carboxylic acid. If the second group is absent, or located in the 4-position, then the reaction takes place much more slowly. The corresponding dianion does not cyclise. A possible explanation[10] is that the second carboxylic acid acts as a proton source to complete the addition reaction. We measured the X-ray crystal structure of **8** to investigate how the carboxylic acid groups interact with the triple bond since this may provide some insight into the mechanism of the cyclisation reaction. Each carboxylic acid group has the possibility of directing an oxygen or a hydrogen atom towards the alkyne. If one oxygen atom and one hydrogen atom from different carboxylic acids were involved in the interaction with the triple bond, this arrangement would model the proposed mechanism.



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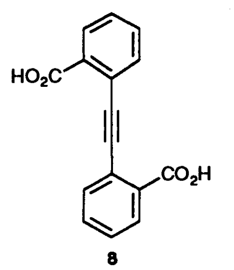

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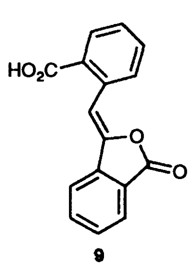

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Results and Discussion

Crystals of **8**, prepared from the dibromo analogue **7**, were grown by slow evaporation of a warm (40 °C) acetic acid solution. Individual crystals for X-ray diffraction studies were examined by photoacoustic Fourier Transform IR spectroscopy to confirm that intramolecular cyclisation had not taken place, and the X-ray crystal structure was measured at 150 K. The molecular structure of **8** is quite remarkable: there is a pair of short intramolecular 1,5 interactions between each carbonyl oxygen atom and the nearer sp carbon atom. Surprisingly, the molecule crystallises with both carboxylic acid groups located to the same side of the triple bond (Fig. 1). Only half the molecule is crystallographically unique, and is related to the second half by a twofold axis lying in the molecular plane and bisecting the triple bond. Details of the molecular geometry are given in Fig. 2. The benzene rings lie at 19.7(1)° to one another and each carboxylic acid group lies at 15.4(1)° to the plane of the attached benzene ring so that the carbonyl oxygen atoms lie 0.984(2) Å out of the average molecular plane. The interactions of the sp carbon atoms with the adjacent carbonyl oxygen

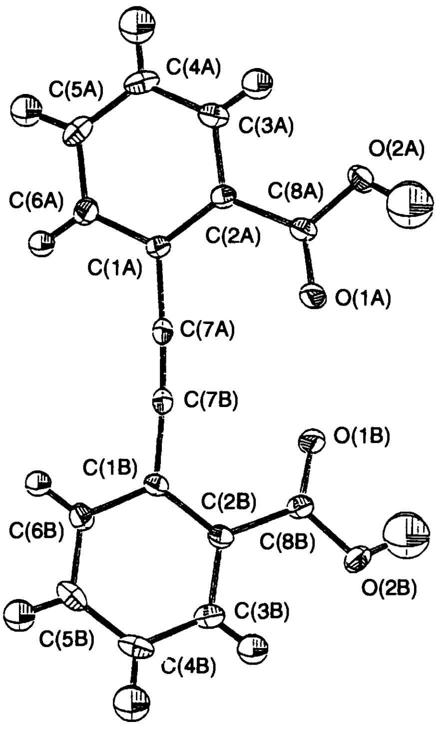


Fig. 1 View of **8** perpendicular to the molecular plane with anisotropic displacement parameters drawn at the 50% level (PLATON)[26]

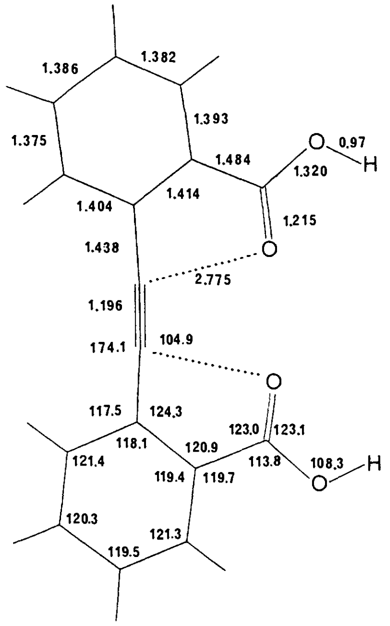


Fig. 2 Selected molecular geometry of **8**. The two halves of the molecule are related by a twofold rotation axis. Esds on interatomic distances (Å) 0.002–0.003 Å (except for the O–H distance, 0.03 Å), esds on interatomic angles (°) 0.2°.

atoms lead to the triple bond being distorted in a unique way. The angles at each sp carbon atom are 174.1(2)° and the torsion angle about the triple bond is −106.1(1)°. This distortion is most easily described as the combination of orthogonal *cis* and *trans* bends. A view from above the molecule (Fig. 1) shows that the triple bond has a *cis* bend in the molecular plane. However, an edge-on view of the molecule (Fig. 3) shows that the triple bond has a *trans* bend in the perpendicular plane. In both views it is clear that the two sp carbon atoms are displaced towards the adjacent carbonyl oxygen atoms, such that the distance between each pair of atoms is only 2.775(2) Å (*ca.* 0.3 Å within the traditional C ··· O van der Waals contact distance). These factors indicate strongly that these are attractive interactions. {An interaction of an ester carbonyl group with an alkyne group has been reported[11] in molecule **10**. In this case, the triple bond is bent from linearity only at the sp carbon atom nearer to the carbonyl oxygen atom [C ··· O: 2.837(2) Å, C–C≡C: 170.5(1)°, O ··· C≡C: 109.7(1)°], since the second sp carbon atom is flanked by two *ortho*-methoxy groups.} Each carboxylic acid group is involved in a pair of intermolecular hydrogen bonds with another carboxylic acid group. This interaction plays an important role in the molecular packing arrangement. The acidic hydrogen atoms are not positionally disordered (as is often the case); the interaction of one carboxylic oxygen atom with the alkyne controls this ordering. The hydrogen bonding links the molecules together to form pairs of parallel strands which lie along the *c* direction [Fig. 4(*a*) and (*b*)].

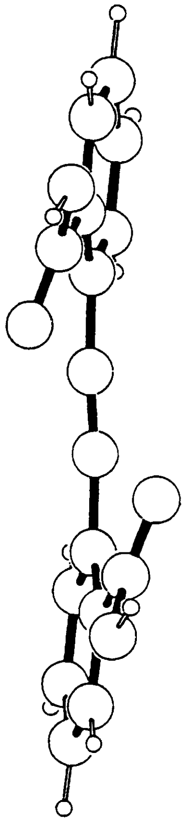


Fig. 3 Edge-on view of **8** (PLUTON)[27]

At each benzene ring in the diacid **8** the substituents are splayed apart in the plane of the ring, more notably at C(1A) and C(1B) (by 3.4°) than at C(2A) and C(2B) (by 0.6°). This pattern of distortions increases the separation between carbonyl oxygen atoms to 3.128(2) Å and widens the O(1) ··· C(7A)≡C(7B) angle to 104.9(1)° similar to that observed in other systems where an electron-rich atom lies close to a triple bond.[5,8,9] This angle of approach allows overlap of the lone pair of the incoming oxygen atom with a lobe of the empty π* antibonding orbital of the triple bond. Calculations support the proposal that the energetically most favoured line of attack lies at *ca.* 125° to a triple bond,[12–14] although there are examples which have no alternative but to adopt a more acute angle of approach, *e.g.* cyclisation of **11** to **12**.[15] In the diacid **8** the reasonably small torsion angle made by the two carbonyl oxygen atoms about the triple bond [36.9(1)°] indicates that a lone pair from each oxygen atom overlap predominantly with the same C,C π* antibonding orbital. Although this is unusual, the alternative in which molecule **8**

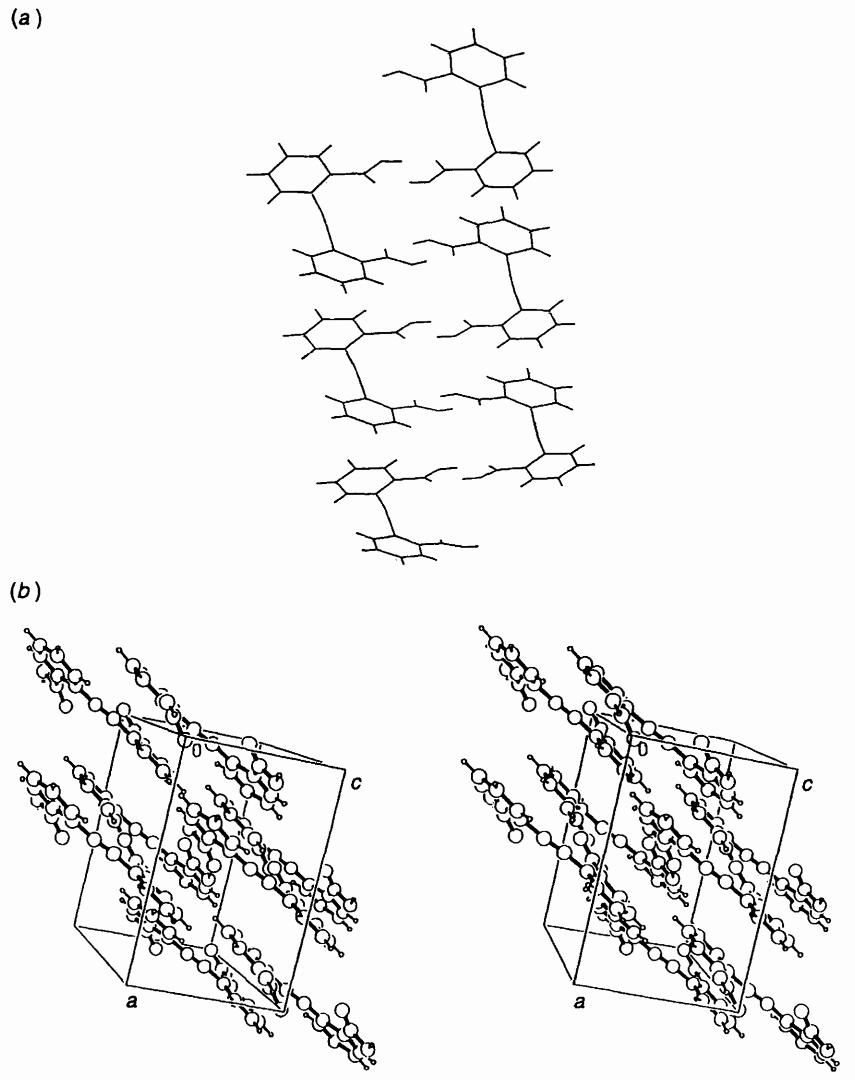
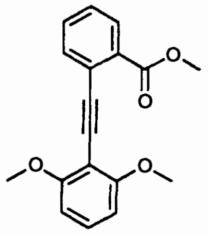


Fig. 4 Crystal packing diagrams for **8** (PLUTON)[27] showing (*a*) a pair of parallel strands of **8**, (*b*) the packing of the strands with axes lying in the *c* direction



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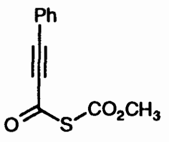

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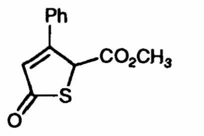

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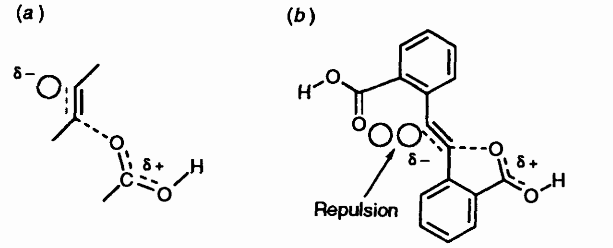

Fig. 5 (*a*) Development of a lone pair on an sp carbon atom as a nucleophile adds to an alkyne; (*b*) repulsion between lone pairs arising in the *trans* conformation of **8**

crystallises with the two O • • • (sp)C interactions oriented in a *trans* arrangement would be expected to be less favourable. The structure of **3** indicates that approach of an oxygen atom to an sp carbon induces the development of a lone pair at the second sp carbon atom whose axis is antiperiplanar to the forming C • • • O bond [Fig. 5(*a*)]. If in **8** the two O • • • C interactions were to be aligned *trans*, each developing lone pair would be oriented towards the lone pair of an incoming oxygen atom [Fig. 5(*b*)]. Further crystal structures of substituted diphenylacetylenes are to be measured, since the significance of a stereoelectronic effect can only be judged from a number of examples. In any one case, it cannot be ruled out that an alternative factor (*e.g.* hydrogen bonding or packing requirements) may be the critical feature in determining a molecule's conformation in the solid state.

The observed distortion of the alkyne group is very unusual. A search for non-linear alkynes in the Cambridge Structural Database[16] (C–C≡C < 176°, R < 0.08, average esd of C,C bonds < 0.01 Å) revealed only one structure, a strained and twisted cyclo-1,7-dialkyne,[17] with C–C≡C–C torsion angles within 40° of those observed for **8**. The pattern of interactions in **8** cannot be a direct pointer to the structure of the transition state for the cyclisation reaction of the corresponding anion. If in the transition state the molecule has a planar conformation with the carboxylic acid and carboxylate groups to the same side of the triple bond then, even allowing for one interaction (of the carboxylate anion) being stronger than the other, there would be two opposing *trans* distortions of the triple bond. In solution, away from the requirement of efficient packing of molecules, such a pair of (unequal) interactions could be involved in the transition state if the phenyl groups were aligned perpendicularly. (The barrier for rotation of the phenyl rings about the molecular axis in diphenylacetylene is estimated to be *ca.* 2.5 kJ mol^{-1}.[18]) Indeed, the crystal structure shows a significant deviation from the coplanar conformation in this direction. This raises the question as to whether the enhanced rate of cyclisation of the anion of **8** is due to a lowering of the energy barrier for addition of the anion to the triple bond by a second C=O $\cdots$ spC attraction, or due to the local availability of a proton to complete the addition as originally proposed. Further kinetic studies on asymmetrically substituted diphenylacetylenes, for example the 2-nitro-2′-carboxylic acid, are planned to distinguish between these two proposals.

The O $\cdots$ C interaction distances in **8** are significantly within the sum of the van der Waals radii of alkyne carbon and carbonyl oxygen atoms (even allowing for the corrections for thermal motion). The former is estimated from spC $\cdots$ spC contacts in crystalline acetylene as 1.78 Å.[19] The latter is estimated from a study[20] of C=O $\cdots$ O=C interactions in the Cambridge Structural Database to be 1.54 Å. Indeed, contact distances in mutual interactions are highly unlikely to be reproduced by a 'fixed radius' model for bonded atoms. For intermolecular interactions it may be possible to develop guidelines for typical distances between a particular pair of atom types using information from the Cambridge Structural Database. However, it is important to note that certain bonded atoms, *e.g.* sulfur and the heavier halogens, act as if they have an ellipsoidal shape.[20,21] Nevertheless, this approach will take account of short contacts owing to attractions between nucleophilic and electrophilic groups, as well as mutual polarisations. Intramolecular contact distances are likely to be further complicated by effects transmitted through the electronic system of the molecule.

Experimental

Preparation of 2,2′-*Ethynylenedibenzoic Acid* **8**.—2,2′-Dibromo-1,1′-ethynylenedibenzene **7** was obtained from 2-bromotoluene in four steps as described[22] except that the product was separated from 1,2-di(2-bromophenyl)ethene by chromatography on silica with hexane as the eluent. Compound **7** (0.44 g, 1.3 mmol) in diethyl ether (10 cm^3) was lithiated with butyllithium (1 cm^3; 2.5 mol dm^{-3} in hexane) and the reaction mixture poured on to solid carbon dioxide as described.[10] The product was obtained as white needles (from acetic acid) m.p. 81 °C; δ_H(270 MHz, CD_3CO_2D) 7.37 (dt, *J* 7 Hz) and 7.52 (dt, *J* 7 Hz) (4-,5-H), 7.65 (dd, *J* 7 Hz, 6-H) and 8.01 (dd, *J* 7 Hz, 3-H); δ_C(67.8 MHz, CD_3CO_2D) 94.5 (sp C), 125.5, 129.4, 131.9, 132.2, 133.6, 135.4 (Ar-C_6) and 171.5 (C=O); ν_{max}/cm^{-1} (photoacoustic, single crystal): 2800br, 1691, 1593, 1566, 1491, 1418, 1309, 1274 and 757; *m/z* (CI) 284 (100) ($M + NH_3 + H^+$), 267 (60) ($M + H^+$) and 248 (40) ($M - H_2O^+$).

X-Ray Crystallography of **8**.—*Crystal data.* $C_{16}H_{10}O_4$, M_r = 266.3, monoclinic, *C2/c*, a = 11.798(2), b = 13.219(1), c = 7.892(1) Å, β = 90.50(1)°, V = 1230.8(3) Å^3, Z = 4, D_c = 1.44 g cm^{-3}, Mo-Kα (λ = 0.710 69 Å), rotating anode, T = 150 K, μ = 0.97 cm^{-1}, max. ($\sin\theta/\lambda$) = 0.70 Å^{-1}, 3243 measured reflections, 1590 unique reflections, 844 reflections with $I > 3\sigma(I)$, final R = 0.038 and R_w = 0.039.

Data collection was performed on a Delft Instruments FAST TV area detector diffractometer as described previously.[23] The structure was solved by direct methods (SHELXS-86[24]) and refined by full-matrix least-squares refinement on *F* (SHELX 76[25]) using anisotropic displacement parameters for non-hydrogen atoms. All hydrogen atoms were located in difference Fourier maps and refined with isotropic displacement parameters. The structure converged at R = 0.038, R_w = 0.039 with a weighting scheme $w^{-1} = [\sigma^2(F) + 0.0011F^2]$. The largest values of Δ/σ in the final cycle of refinement were 0.002 (for non-hydrogen atoms) and 0.007 (hydrogen atoms), and the maximum and minimum peaks in the final difference electron density map were 2.7 and -1.8 e Å^{-3}. Atomic coordinates and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre.*

Acknowledgements

We are very grateful to Professor M. B. Hursthouse and the SERC X-Ray Crystallography service for collecting the dataset, and to Dr. D. V. Bowen and the Physical Sciences Laboratory of Pfizers Ltd., Sandwich for spectroscopic data, most notably the photoacoustic IR data. Furthermore, we thank the University of Kent for a studentship (M. P.) and for further financial support.

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* For details of the CCDC deposition scheme, see 'Instructions for Authors (1994),' *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1.

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Paper 4/02631D
Received 4*th May* 1994
Accepted 19*th July* 1994