

Geometry distorting intramolecular interactions to an alkyne group in 1-(2-aminophenyl)-2-(2-nitrophenyl)ethyne: a joint experimental-theoretical study

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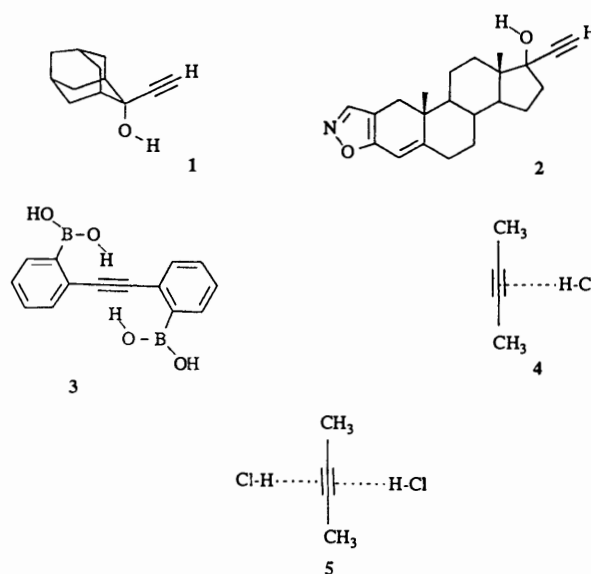
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X-Ray diffraction studies on the title compound show that in the crystalline state the amino and nitro groups lie to the same side of the triple bond and are hydrogen bonded to each other. There is a short contact to each alkyne carbon atom; one from a nitro oxygen atom, which leads to a *trans* bend in the alkyne, and one from an amino hydrogen atom. The analyses of the *ab initio* electron densities for this molecule and for its conformer with functional groups lying on opposite sides of the triple bond, using the theory of atoms in molecules, indicate that in both cases there is a bond path and associated (3, -1) critical point between the nitro oxygen atom and the nearer alkyne carbon atom, but not between the amino hydrogen atom and its alkyne carbon neighbour. Plots of the Laplacian for both conformers indicate local concentrations of 'lone-pair' density on the nitro oxygen atom, with local depletions in the valence shell charge concentration on the alkyne carbon atom, indicative of a nucleophile/electrophile type interaction. The geometry of the interaction of the alkyne with the amino hydrogen atom is far from optimal in the *trans* conformer.

Introduction

Alkyne groups can react with electrophiles or nucleophiles depending on the electronic effects of the terminal substituents. For example, but-3-yne adds one equivalent of bromine,¹ whereas the electron-deficient alkynes methyl propiolate and dimethyl but-2-yne-1,4-dioate add aziridine.² Tolan (diphenylethyne) occupies an intermediate position, reacting with both electrophiles and nucleophiles. Thus it will add chlorine³ or bromine⁴ as well as adding thiols,⁵ tributylphosphine (to give a betaine)⁶ and butyllithium.⁷

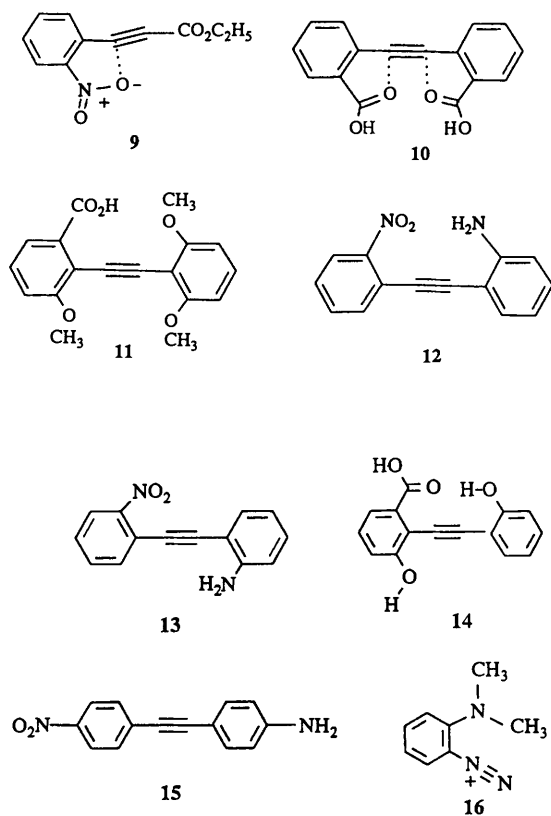
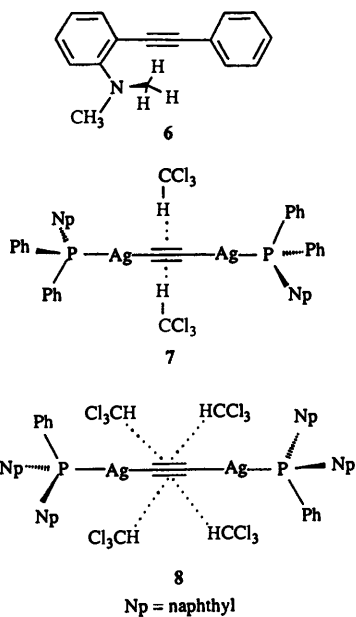
Similar trends are observed for the through-space interactions of alkynes with functional groups *viz.* on the one hand, there are cases where alkynes make hydrogen bonds with O-H groups, for example intermolecular O-H...spC bonds in the crystal structures of the derivatives **1**⁸ and **2**⁹ containing the ethynylmethanol moiety, and intramolecular (bifurcated) B-O-H...spC hydrogen bonds in the diboronic acid **3** [H...spC, 2.51(2) Å].¹⁰ Similarly, the 1:1 and 1:2 complexes of the but-2-yne with hydrogen chloride, **4** and **5**, show short Cl-H...spC contacts [2.36(3)–2.43(3) Å],¹¹ and a short H...spC contact [2.39(3) Å] has even been observed between a *N*-methyl group and an alkyne carbon in the crystal structure of **6** at 98 K.¹² A recent report concerning the structures of **7** and **8**, two ethynyl gold complexes, showed short contacts between the alkyne group and two or four chloroform molecules respectively,¹³ and examples of attractive close contacts between the spC-H atom of terminal alkynes and alkyne bonds have been reported (2.60–2.77 Å).^{14,15} In general these interactions do not perturb the linear geometry of the alkyne significantly. Rzepa *et al.*¹⁶ have calculated the O-H...spC interaction to be worth *ca.* -1.5 kcal mol⁻¹ by semi-empirical methods and Steiner *et al.*¹⁵ have calculated the spC-H...spC interaction at *ca.* -0.9 kcal mol⁻¹, but that a further gain of -0.5 kcal mol⁻¹ is achieved when the interactions are organised in a cooperative fashion.†



On the other hand, there are cases where an electron rich atom makes a close contact with an electron deficient alkyne group. For example, the alkyne **9** shows a short (1,5) contact between a nitro oxygen atom and a spC atom [O...C, 2.642(2) Å] and an induced *trans* bend in the alkyne group, such that the spC atom involved in the shorter contact to the oxygen atom is displaced towards the oxygen atom.¹⁷ Similar attractive interactions are observed in the dicarboxylic acid **10** between each carbonyl oxygen atom and the nearer alkyne carbon atom [O...C, 2.775(2) Å]¹⁸ and in carboxylic acid **11** [O...C, 2.785(2) Å].¹⁹

We now report on the synthesis of **12**, its experimental geometry as determined by single crystal X-ray diffraction and the calculated geometries and electronic structures of **12** and its conformational *trans* isomer **13** obtained by *ab initio* molecular

† 1 cal = 4.184 J.



orbital techniques. This molecule has an alkyne bond with the potential to make contacts with both an electron rich oxygen atom and an electron poor hydrogen atom, and may provide a useful model for an early stage in the addition of a nucleophile and proton to an alkyne. This reaction, for secondary amines such as aziridine, gives mainly the *trans* product in protic solvents while in aprotic solvents the *cis* product is produced.^{20,21}

As previously outlined,¹⁸ it may be expected that the nucleophilic approach of the oxygen atom to the triple bond will cause a change in the electronic structure such that the electrophilic sp carbon atom will take on partial sp² character. Likewise the other alkyne carbon atom may move towards sp² character possessing an incipient lone pair of electrons *trans* to the approaching nucleophile. If this molecule were to adopt the *trans* conformation 13, the interactions should be cooperative,

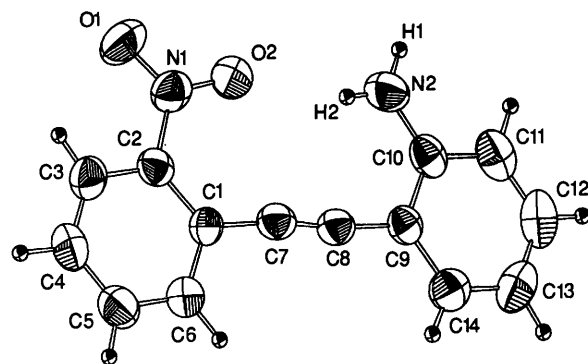


Fig. 1 Molecular structure of 12 in the crystalline state as determined by X-ray diffraction, showing molecule A with anisotropic displacement parameters drawn at the 50% level for non-H atoms and using spheres of a fixed radius for H-atoms⁴⁰

Table 1 Measured bond lengths (Å) for molecules A and B of 12 and calculated bond lengths for 12, its *trans* conformational isomer 13, and for unsubstituted tolan

Bond	A	B	12	13	Tolan
O(1)–N(1)	1.226(3)	1.225(3)	1.193	1.196	—
O(2)–N(1)	1.222(3)	1.214(3)	1.194	1.190	—
N(1)–C(2)	1.469(4)	1.466(4)	1.466	1.468	—
N(2)–C(10)	1.370(4)	1.368(4)	1.352	1.360	—
C(1)–C(2)	1.397(4)	1.397(4)	1.399	1.399	1.395
C(1)–C(6)	1.407(4)	1.402(4)	1.401	1.400	1.395
C(1)–C(7)	1.428(4)	1.432(4)	1.434	1.435	1.442
C(2)–C(3)	1.386(4)	1.384(4)	1.388	1.386	1.384
C(3)–C(4)	1.368(5)	1.370(5)	1.379	1.380	1.387
C(4)–C(5)	1.385(5)	1.390(5)	1.389	1.388	1.387
C(5)–C(6)	1.372(4)	1.370(5)	1.380	1.381	1.384
C(7)–C(8)	1.201(4)	1.200(4)	1.192	1.192	1.191
C(8)–C(9)	1.419(4)	1.421(4)	1.434	1.436	1.442
C(9)–C(10)	1.410(4)	1.408(4)	1.412	1.408	1.395
C(9)–C(14)	1.398(4)	1.402(4)	1.398	1.399	1.395
C(10)–C(11)	1.391(5)	1.399(5)	1.407	1.403	1.384
C(11)–C(12)	1.366(5)	1.376(5)	1.376	1.378	1.387
C(12)–C(13)	1.388(6)	1.388(5)	1.395	1.394	1.387
C(13)–C(14)	1.377(5)	1.381(5)	1.376	1.377	1.384

with the incipient lone-pair enhancing the interaction to the hydrogen atom. This conjecture is investigated by determining the atomic interaction lines, the values of the density and its eigenvalues at the bond critical points, and the Laplacian of the one-particle electron density [$\nabla^2\rho(r)$].

Results

Crystallographic data

The molecule was synthesised from (2-nitrophenyl)ethyne²² and 2-iodoaniline with a Pd^{II}/Cu^I catalytic system.²³ The room temperature X-ray diffraction experiment reveals two crystallographically unique molecules, A and B, which have very similar molecular geometries. The experimental structure of molecule A and the atomic numbering scheme is shown in Fig. 1. Bond lengths and angles are presented in Tables 1 and 2. The structure of molecule A will be discussed in detail with the corresponding data for molecule B in square brackets. The close intramolecular contacts are indicated in Fig. 2. The carbon skeleton is nearly planar, with only a small angle, 3.6(2)° [5.1(2)°], between the best planes of the two phenyl rings. The plane of the nitro group lies only 5.1(5)° [6.9(6)°] out of the plane of the attached aromatic ring. Most notable is the *cis* arrangement of the amino and nitro groups about the molecular axis, and the intramolecular N(2)–H(2)···O(2)–N(1) hydrogen bond between them which lies nearly parallel to the triple bond. This hydrogen bond is of length 2.34(4) Å [2.37(4) Å] with an

Table 2 Measured bond angles (°) for molecules A and B of **12** and calculated bond angles for **12**, its *trans* conformational isomer **13** and unsubstituted tolan

Bond angle	A	B	12	13	Tolan
O(1)–N(1)–O(2)	121.6(3)	122.0(3)	124.9	125.5	—
O(1)–N(1)–C(2)	118.8(3)	118.2(3)	116.9	116.6	—
O(2)–N(1)–C(2)	119.6(3)	119.8(3)	118.2	117.9	—
C(2)–C(1)–C(6)	116.2(3)	116.2(3)	116.9	116.9	119.3
C(2)–C(1)–C(7)	126.2(3)	126.0(3)	125.7	125.1	120.3
C(6)–C(1)–C(7)	117.7(3)	117.8(3)	117.4	117.9	120.3
C(1)–C(2)–C(3)	122.2(3)	122.5(3)	121.7	121.7	120.2
N(1)–C(2)–C(3)	116.8(3)	117.0(3)	116.2	116.4	—
N(1)–C(2)–C(1)	121.0(3)	120.6(3)	122.1	121.9	—
C(2)–C(3)–C(4)	119.9(3)	119.3(3)	120.1	120.1	120.2
C(3)–C(4)–C(5)	119.5(4)	119.8(4)	119.3	119.4	119.9
C(4)–C(5)–C(6)	120.6(4)	120.4(4)	120.4	120.3	120.2
C(1)–C(6)–C(5)	121.5(3)	121.8(3)	121.5	121.6	120.2
C(1)–C(7)–C(8)	171.9(3)	172.4(3)	174.5	176.6	180.0
C(7)–C(8)–C(9)	173.4(3)	173.5(3)	174.8	174.6	180.0
C(10)–C(9)–C(14)	119.6(3)	120.2(3)	120.1	120.0	119.3
C(8)–C(9)–C(14)	121.9(3)	120.7(3)	121.1	118.9	120.3
C(8)–C(9)–C(10)	118.5(3)	119.1(3)	118.9	121.1	120.3
N(2)–C(10)–C(9)	120.7(3)	120.4(3)	121.2	121.0	—
N(2)–C(10)–C(11)	120.8(4)	121.4(4)	121.0	120.9	—
C(9)–C(10)–C(11)	118.5(3)	118.2(3)	117.7	118.0	120.2
C(10)–C(11)–C(12)	121.0(4)	120.6(4)	120.8	120.7	120.2
C(11)–C(12)–C(13)	121.1(4)	121.6(4)	121.5	121.4	119.9
C(12)–C(13)–C(14)	119.0(4)	118.7(4)	118.4	118.5	120.2
C(9)–C(14)–C(13)	120.8(4)	120.7(4)	121.5	121.3	120.2

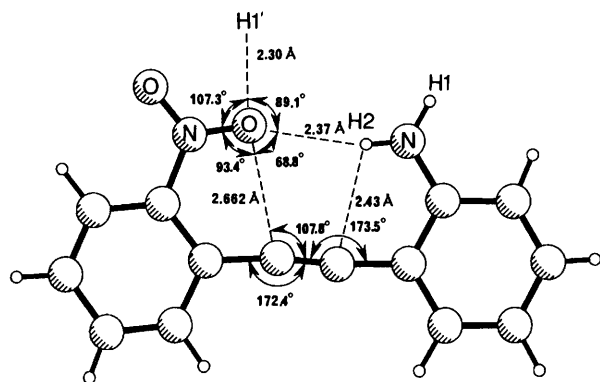


Fig. 2 Details of the geometry of the close contacts involving the nitro, amino and alkyne groups in molecule A of the experimentally determined crystal structure of **12**; distances in Å, angles in °. Estimated standard deviations for distances and angles involving only non-H atoms: 0.004 Å and 0.3°; for distances and angles involving H atoms: 0.04 Å and 1.5°. ⁴¹

angle at the bridging hydrogen atom of 164(3)° [156(3)°]. The separation, which is at the upper limit of the range for N–H...O hydrogen bonds, is controlled by the molecular geometry. Both of the atoms involved lie close to the alkyne carbon atoms C(7) and C(8). The O(2)...C(7) distance is 2.672(4) Å [2.662(4) Å] which is *ca.* 0.45 Å within the sum of the van der Waals radii. The alkyne is bent in a *trans* mode by 8.1(3)° [7.6(3)°] at C(7), and by 6.6(3)° [6.5(3)°] at C(8) such that the C(7) atom is displaced towards O(2) atom. The O(2)...C(7)≡C(8) angle is 108.3(2)° [107.8(2)°]. These distortions are similar to those observed in alkyne **9** [O...C, 2.642(2) Å, O...C≡C 106.4(2)°]. The amino hydrogen atom H(2) lies close to the alkyne C(8) atom at a distance of 2.42(4) Å [2.43(4) Å] which is *ca.* 0.5 Å within the sum of the relevant van der Waals radii, and similar in length to other H...spC close contacts.^{8–12} The interaction of the nitro oxygen atom is responsible for the *trans* bending of the alkyne; hydrogen bonding to an alkyne does not induce a significant change in bonding geometry. Similar results²⁴ have been reported for the 2,6,2'-trisubstituted tolan **14** which shows an intramolecular

hydrogen bond between a phenolic H atom and a carbonyl O atom aligned parallel to the triple bond (2.01 Å).[‡]

The in-plane angular displacements of the substituents at each benzene ring are quite different. The nitro and alkyne groups are displaced apart, more notably at C(1), whilst the amino and alkyne groups are displaced slightly towards each other, more notably at C(9). The difference is due to the larger size of the oxygen atom compared with the hydrogen atom.

Each molecule is part of a centrosymmetrically related pair of (N)O...H(N) hydrogen bonds (Fig. 3). These involve the same oxygen atom, O(2), which takes part in intramolecular hydrogen bonding, but the second amine hydrogen atom, H(1), which is not involved in the intramolecular bond {H(1)'...O(2), 2.42(4) Å [2.30(4) Å]; N(2)'–H(1)'...O(2), 101(2)° [107(2)°]}. Thus, the nitro oxygen atom, O(2), is involved in interactions with three other atoms, one sp carbon atom and two hydrogen atoms. The angular dispositions of these interactions are shown in Fig. 2. The crystal packing arrangement is shown in Fig. 3.

Partial *o*-quinoid character in each benzene ring is suggested by two shorter bonds in each ring [C(3)–C(4) and C(5)–C(6); C(11)–C(12) and C(12)–C(13)] which is to be expected; similar effects are seen in the structure of the *para*-isomer **15**²⁵ and, to a greater degree, in the structure of the 2-dimethylamino-benzenediazonium cation **16**.²⁶ The H₂N–C bonds (1.370 and 1.368 Å) are slightly shorter than the average value for an amino-benzene [1.38(3) Å, as revealed by a search of the Cambridge Structural Database], but the (O₂)N–C bonds (1.469 and 1.466 Å) are close to the typical value [1.47(2) Å].²⁷ The lengths of these two bond types are similar to those in the *para*-isomer **15**.

While the crystallographic data has identified an interaction which distorts the linear geometry of the alkyne, no clue as to the nature of this interaction is obtained. Also, as the conformation is experimentally found to be *cis* the conjecture that the amino hydrogen atom will act as an electron acceptor, cooperatively enhancing the distortion due to the nitro oxygen cannot be furthered from the geometrical parameters obtained from experiment. Further information on these two topics has been obtained from theoretical *ab initio* calculations.

Calculations

The gas-phase geometry optimisations of the *cis* and *trans* forms **12** and **13** reproduce the experimental geometries acceptably well with perhaps the exception of O(1)–N(1), O(2)–N(1) and N(2)–C(10) bonds, and the angles within the nitro group. Despite the limited quality of the basis set the main geometrical features such as the distortion of the alkyne from linearity and the trends in the C–C bond lengths in the aromatic rings are reproduced, as inspection of Tables 1 and 2 testifies. The *cis* conformation **12**, as experimentally found, is almost certainly due to the intramolecular hydrogen bond between H(2) and O(2); single point calculations using the 6-31G** basis at the optimised geometries give an energy difference of 12.620 kJ mol^{–1} in favour of the *cis* isomer.

Topological analysis of the electron density has become established as a fundamental tool for the extraction of chemically useful information from molecular wavefunctions. A full development of the theory may be found in Bader's treatise,²⁸ however it is instructive to review the relevant features here. Critical points (CPs) in the scalar field of $\rho(\mathbf{r})$ are defined as those points where the first derivatives of the density vanish, *i.e.* eqn. (1). The matrix of partial second derivatives of

$$\nabla\rho(\mathbf{r}) = i\frac{\partial\rho(\mathbf{r})}{\partial x} + j\frac{\partial\rho(\mathbf{r})}{\partial y} + k\frac{\partial\rho(\mathbf{r})}{\partial z} = 0 \quad (1)$$

the density at any point, called the Hessian, is a real symmetric

[‡] Incorrectly reported as 2.973 Å.

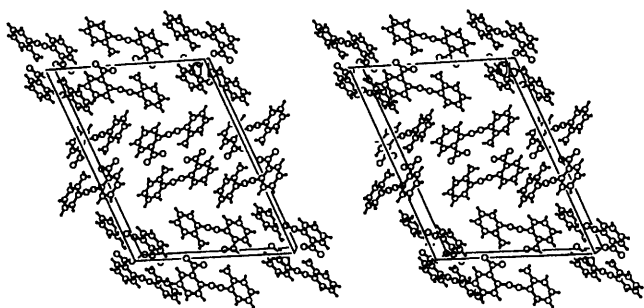


Fig. 3 Stereoview of the crystal packing arrangement of the centrosymmetric dimers of **12** (PLUTON ⁴¹)

Table 3 Mulliken charges (electrons)

Moiety	12	13
-NH ₂	-0.161	-0.207
NH ₂ -Ar	+0.325	+0.386
-NO ₂	-0.461	-0.447
NO ₂ -Ar	+0.453	+0.451
C(7)	-0.111	-0.064
C(8)	-0.055	-0.120

third-order square array, and as such may be diagonalised to yield three real eigenvalues and associated eigenvectors, the latter being the principal curvatures of the density. The topological properties of a CP are summarised by the rank (ω), the number of non-zero eigenvalues of the Hessian, and its signature (σ), the arithmetic sum of the signs of its eigenvalues. Local maxima (nuclear positions) behave as (3, -3) CPs, and it is the manner in which these are linked by atomic interaction lines, passing through (3, -1) CPs (bond critical points) which unequivocally defines the system of interactions present in the molecule. The physical properties such as the density itself $\rho(\mathbf{r})$, the ratio of the negative eigenvalues of the Hessian expressed as the ellipticity $\varepsilon = [(\lambda_2/\lambda_3) - 1]$ and especially the Laplacian $\nabla^2\rho(\mathbf{r})$ evaluated at the bond CPs give quantitative and comparable information on the strength and other characteristics of the atomic interaction. In terms of the interactions to the alkyne carbon atoms with either O(2) or H(2), the principle feature to be identified in the topology of $\rho(\mathbf{r})$ is a (3, -1) bond CP. Figs. 4(a), (b) and (c) show the Laplacian overlain with those gradient vectors of the density, $\nabla\rho(\mathbf{r})$ which coincide with bond critical points, for the *cis*, *trans* and tolan forms. These are obtained by evaluating the vector $\nabla\rho(\mathbf{r})$, moving a small distance along this vector, re-evaluating it and so on until either a minimum or maximum is reached. If the process is started at a (3, -1) CP and moving in the direction of increasing $\rho(\mathbf{r})$ then the two parts of the bond path are traced; if moving toward lower $\rho(\mathbf{r})$ then the atomic boundary is traced. (3, -1) CPs are shown on the diagram as bold dots. It can be observed that there does indeed exist a bond CP between O(2) and C(7) in both conformers and the bond paths may easily be followed. Likewise for the hydrogen bond between O(2) and H(2) in the *cis* form. However no such bond path is found between H(2) and C(8) in either form strongly indicating that no direct interaction is present here. This is particularly important in the case of the *trans* molecule and rules out the participation of the hydrogen atom in accepting density from the alkyne carbon atom.

The Laplacian of the density $\nabla^2\rho(\mathbf{r})$ is of particular interest in the O(2)-C(7) interaction, as it has been shown to be a reliable indicator of local chemical reactivity in molecules.²⁹ In simplistic terms, O(2) may be thought of as 'electron-rich' while alkyne carbon atoms with electron withdrawing substituents such as C(7) may be thought of as 'electron-poor'. The Laplacian of any scalar function indicates local concentrations and depletions of that function. In the case of the electron

density, the Laplacian also has a quantum mechanical meaning, occurring in the expression for the local virial theorem [eqn. (2)],

$$(\hbar^2/4m)\nabla^2\rho(\mathbf{r}) = 2G(\mathbf{r}) + V(\mathbf{r}) \quad (2)$$

where $G(\mathbf{r})$ is the kinetic energy density and $V(\mathbf{r})$ is the potential energy density, the sum of which give the total electronic energy density $E(\mathbf{r})$. While the virial theorem, $2T(\Omega) = -V(\Omega)$, must be satisfied globally either over the whole molecule or a correctly defined atomic volume (Ω) it need not be satisfied locally. Those places where the Laplacian has a negative value indicate local concentration of charge density and also a local dominance of electronic potential over kinetic energy relative to the global virial ratio of 2:1. It has been observed that while chemical 'lone-pairs' do not reveal themselves in the total density, they do appear as volumes of negative Laplacian and hence are places where the potential energy is locally dominant. In general, nucleophiles are found to possess regions of negative Laplacian and electrophiles regions of positive Laplacian. The simplistic conception of electron rich and electron poor atoms could well be better interpreted as atoms displaying regions of negative and positive Laplacian respectively, reacting in such a way as to allow electron flow from compressed regions to rarified regions and to move toward local satisfaction of the virial theorem. The Laplacians in the central regions of **12**, **13** and tolan show that for the O(2)-C(7) interaction the lone pair region of the nitro oxygen lines up approximately with the depletion in the valence shell charge concentration (VSCC) of the carbon atom. This seems to indicate a potential nucleophile/electrophile type interaction. Since the Laplacian occurs in the quantum expression for the virial theorem, it indicates the full quantum potential as opposed to only the classical electrostatic part and hence this arrangement of local depletions and concentrations of charge signifies an attractive interaction. Interestingly, in the molecular plane the depletions of the VSCC of C(7) appear to be more severe than in the tolan molecule, while those of C(8) are less so. This would accord with the idea that the benzene ring with the electron withdrawing nitro group pulls density from C(7) while the electron donating amino group enhances the density on C(8). However, in the perpendicular plane, the depletion and enhancement are the other way around, and if the push-pull effect expressed itself through the π -system the effect should be in the same direction as in the case of the molecular plane and have a greater degree. A Mulliken charge analysis of the relevant atoms (Table 3) does not indicate any substantial movement of electrons around the molecule. A more likely explanation is that electron-electron repulsions exerted on C(7) by the density of O(2) in the molecular plane cause a redistribution of charge towards C(8) in the plane and out of the plane on C(7). If an incipient lone pair were present on C(8) it should manifest itself as a (3, -3) CP in the Laplacian itself. No such feature is observed.

The topological nature of weak bonds observed in both charge transfer and steric interactions has recently been investigated by Cioslowski *et al.*³⁰ The values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ in the O(2)-C(7) interactions studied here (Table 4) have similar characteristics to those presented; the Laplacian is positive at the critical point denoting a non-covalent, closed shell interaction, and the value of the density itself is low. The values of the ellipticity are high in the interactions investigated here which by Cioslowski's criteria would indicate a charge-transfer interaction, however we feel that these criteria are not general to molecular interactions of arbitrary arrangement.

The observation of a 'short contact' from a structural measurement has often been ascribed to some particular sort of attraction between the atoms involved. While in many cases this may be so, it is not a sufficient condition. Other energetically favourable factors, especially in a crystal structure, can outweigh the unfavourable repulsive energy produced by forcing two atoms close together. The observation of a

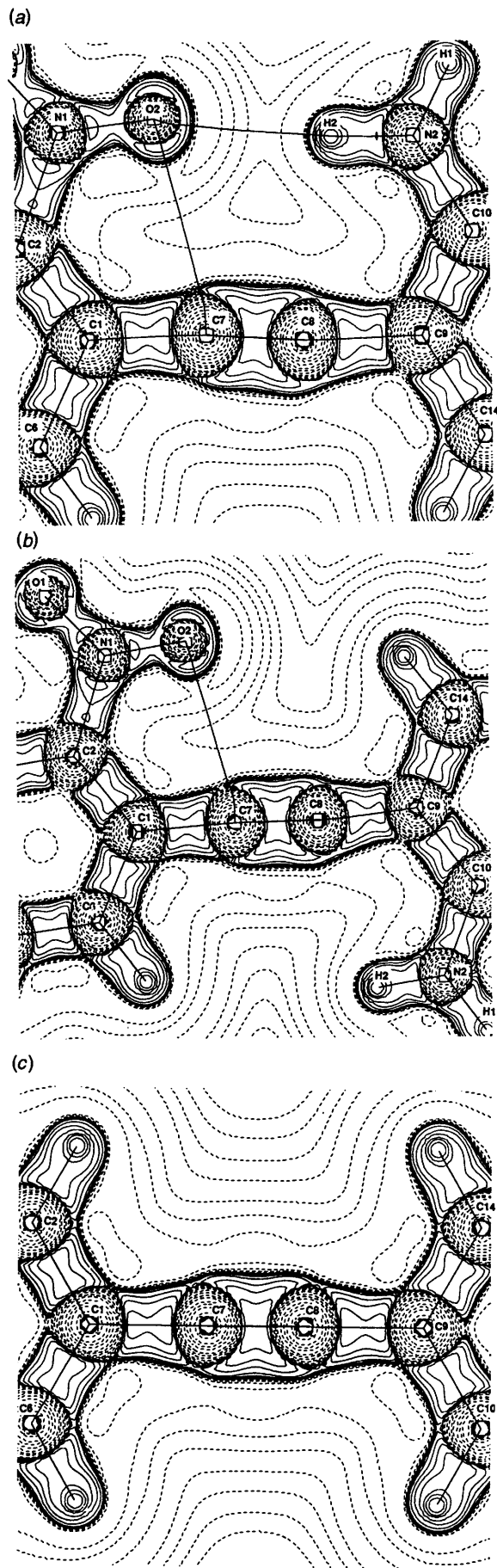


Fig. 4 Plots of the Laplacian overlay with bond paths and atomic boundaries for the calculated electron densities for (a) the *cis* isomer **12**, (b) the *trans* isomer **13** and (c) tolan

Table 4 Critical point analyses

Bond	$\rho/e \text{ bohr}^{-3}$	$\nabla^2\rho/e \text{ bohr}^{-5}$	ϵ
H(2) ... O(2)	0.0118	0.0468	0.0556
O(2) ... C(7) 12	0.0173	0.0633	0.2797
O(2) ... C(7) 13	0.0178	0.0660	0.2726

structural distortion accompanying an interaction can give further evidence as to the nature of the interaction. This is the case for the adjacent nitro oxygen and the alkyne carbon atom in **12**, where the triple bond has distorted to move the 'attacked' carbon atom nearer to the nitro oxygen atom. Furthermore, it is satisfying to observe that the analysis of the calculated electron density also identifies a bond path between these two atoms. In contrast, the close contact between an amino hydrogen atom and an alkyne carbon atom could lead to this being ascribed as due to a H- π hydrogen bond. Yet the calculations do not support this. The optimal geometry for such a hydrogen bond would place the hydrogen atom in the plane bisecting the triple bond, yet in **12** or *trans* conformer **13** the hydrogen atom lies *ca.* 1 Å out of the plane. The degree of 'attack' of the nitro oxygen atom on the triple bond represented in the structures of **12** and **13** is insufficient for the development of significant lone-pair density at the second alkyne carbon atom.

Experimental

Preparation of **12**

Copper(I) iodide (4.4 mg, 0.28 mmol), bis(triphenylphosphine)palladium dichloride (19 mg, 0.28 mmol) and 2-iodoaniline (0.61 g, 2.8 mmol) were added to triethylamine (10 ml) under nitrogen and with sonication. 2-Nitrophenylethyne **22** (0.4 g, 2.8 mmol) in triethylamine (6.3 ml) was added dropwise and after 5 min a blood red precipitate appeared. Sonication was continued for a further 10 min and after heating to 80 °C for 10–15 min, the blood red solid disappeared and a yellow solid in a dark red solution was produced. Triethylamine was removed *in vacuo*, the residue dissolved in diethyl ether (60 ml), filtered through Celite, washed with water (10 ml) and then dried (MgSO₄). Evaporation of the solvent gave 1-(2'-aminophenyl)-2-(2''-nitrophenyl)ethyne **12** (0.32 g, 48%) as red crystals (from hexane-dichloromethane), mp 112–115 °C (Found: C, 70.6; H, 4.1; N, 11.7%. C₁₄H₁₀N₂O₂ requires C, 70.6; H, 4.2; N, 11.8%); δ_{H} (270 MHz, CDCl₃) 8.14 (1 H, d, *J* 8.5, § 3'-H), 7.73 (1 H, dd, *J* 9.1 and 1, 6'-H), 7.60 (1 H, dt, *J* 7.4 and 1, 5'-H), 7.41 (1 H, t, *J* 7.1, 4'-H and 1 H, d, *J* 7.1, 6''-H), 7.18 (1 H, dt, *J* 7.1 and 1, 4''-H), 6.70 (1 H, d, *J* 8.2, 3''-H and 1 H, t, *J* 7.7, 5''-H), 4.69 (2 H, br s, NH₂); δ_{C} (270 MHz, CDCl₃) 148.92 (C-2'), 147.7 (C-2''), 134.3, 132.6, 132.0, 130.5, 127.6, 124.5, 118.8, 117.0, 113.8, 105.6 (10 × ArC), 94.7 and 90.2 (2 × spC); ν_{max} /cm⁻¹ 3390 and 3440 (NH₂), 2186 (C≡C), 1614; *m/z* (EI) 239 (M + H⁺, 100%), 223 (15), 209 (20), 137 (25), 120 (45); λ_{max} (CH₃OH)/nm 251 (ϵ /dm³ mol⁻¹ cm⁻¹ 11 500), 256 (10 200), 259 (14 700), 262 (11 000), 264 (11 700), 267 (11 600), 271 (13 300), 273 (11 200), 276 (14 200), 285 (20 100), 289 (21 300), 324 (12 800), 383 (10 100).

Structure determination

Crystal Data. C₁₄H₁₀N₂O₂, *M* = 238.26; monoclinic; *a* = 24.445(4), *b* = 5.647(1), *c* = 18.584(3) Å; β = 111.5(1)°; *V* = 2386.5 Å³ determined by least squares fit to the setting angles of 38 reflections in the θ range 5.019–12.268°; Mo-K α (λ = 0.71069 Å); *P*2₁/*c*; *Z* = 8; *D*_x = 1.33 g cm⁻³; deep red tablet.

§ *J* Values are given in Hz.

shaped crystal, approx. dimensions $0.4 \times 0.35 \times 0.15$ mm; $\mu = 0.9 \text{ cm}^{-1}$. ¶

Data Collection and Processing. Thick red needles of **12** were grown from a methanol solution. [Recrystallisation from a hexane-dichloromethane (1:1) solution gave red needles and also a microcrystalline pale yellow solid.] X-Ray diffraction data were collected at room temperature on a Siemens P4 automated diffractometer in θ - 2θ mode to resolution $[(\sin\theta/\lambda)_{\text{max}}] = 0.59 \text{ \AA}^{-1}$ yielding 3457 unique reflections, 2069 reflections with $F_o \geq 4\sigma(F)$. Attempts to collect low temperature data failed due to the samples shattering on cooling at ca. 250 K.

Structure Analysis. The structure was solved by direct methods using SHELXS-86³¹ and refined with SHELXL-93³² using anisotropic displacement parameters for non-hydrogen atoms, and isotropic displacement parameters for hydrogen atoms, all of which were located from difference Fourier maps. The refinement converged using a weighting scheme: $w^{-1} = \sigma^2(F_o^2) + (0.0532P)^2$ where $P = [(larger\ of\ F^2\ or\ 0) + 2F_c^2]/3$, with an R value of 0.053 for data with $F_o \geq 4\sigma(F_o)$, a weighted wR value of 0.156 for all data, a mean shift/ESD of 0.041 and a maximum shift/ESD of 0.172 [$U(11)$ of $O(1A)$]. The maximum and minimum peaks of electron density in the final difference Fourier map were 0.15 and -0.17 e \AA^{-3} . ¶

Computation

All theoretical calculations utilised the GAMESS³³ package, running on a DEC Alpha C workstation and a cluster of Hewlett-Packard UNIX workstations. Due to the large size of these molecules, the Direct SCF technique was used for all calculations. For the *cis* isomer, the geometry was optimised utilising a custom basis set, 3-21G(d), consisting of the preprogrammed 3-21G functions³⁴ supplemented by a single shell of six cartesian *d*-functions³⁵ on each non-hydrogen centre and taking the experimentally determined geometry as the starting point. This has no true symmetry, but is approximately planar. After 12 cycles of optimisation the structure had become almost exactly planar so the geometry was constrained to planarity in order to take advantage of the substantial benefits of the use of symmetry in the integral evaluation routines. The *trans* isomer used the same 3-21G(d) basis set for the geometry optimisation and was again constrained to planarity. After convergence, single point calculations at the higher 6-31G** level^{36,37} of theory were performed at the 3-21G(d) geometries [6-31G**/3-21G(d)] to establish a more reliable estimate of the gas-phase energies and electron densities.

The topological analysis of the electron density was performed by the SADDLE and GRDVEC programs from the AIMPAC³⁸ suite of programs; searches of the Laplacian utilised the BUFFALO³⁹ program.

¶ Atomic coordinates and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and reference number 188/18.

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