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Amine–Nitrile Hydrogen Bonding: Tetracyanoethylene as Electron Donor in the Carbazole–Tetracyanoethylene 1:2 Complex

John Masnovi,* Ronald J. Baker,*,† Robert L. R. Towns, and Zhenhua Chen

Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115

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The crystal and molecular structure of the carbazole–tetracyanoethylene (TCNE) molecular complex is examined by single-crystal X-ray diffraction. The complex crystallizes in the monoclinic space group $P2_1/n$, $a = 7.273$ Å, $b = 6.129$ Å, $c = 22.942$ Å, $\beta = 95.76°$, $V = 1017.5$ Å^3, $Z = 4$, final residual values $R = 0.067$, $R_w = 0.058$. The complex in the solid state has the unusual stoichiometry 1 carbazole:2 TCNE. The carbazole is centrosymmetrically disordered about the origin of the unit cell and participates in intermolecular hydrogen bonding between the amino hydrogen (H9) of carbazole and a nitrile lone electron pair of TCNE with angles (carbazole) N9–H9···NT5 (TCNE) 168° and (carbazole) H9···NT5≡CT5 (TCNE) 156°, distance (carbazole) N9···NT5 (TCNE) 3.155 Å. Additionally, apparent π interactions involving carbazole and TCNE are less extensive than in related complexes.

Poly(9-vinylcarbazole) is one of the most useful conducting organic polymers.[1] In the presence of electron-accepting dopants such as tetracyanoethylene (TCNE), polyvinylcarbazole becomes a photoconductor.[2] In the course of our investigations into the relationship between structural properties, photoconductivity, and reactivity,[3] we have determined the structure of the crystalline complex formed between carbazole and TCNE by single-crystal X-ray diffraction. Carbazole forms a weak 1:1 complex with TCNE in solution.[4] However, the complex in the solid state was found to contain two TCNE molecules for each carbazole present, with an intermolecular hydrogen bond between the amino hydrogen of carbazole and a nitrile nitrogen of TCNE. The hydrogen bond in this structure closely resembles the stronger hydrogen bonds observed with more activated amines and nitriles.[5-7]

Experimental Section

A dark blue crystal of dimensions 0.46 × 0.39 × 0.14 mm grown from CH_2Cl_2 by slow evaporation was mounted on a glass fiber and coated with quick-drying epoxy in order to retard decay in crystalline integrity as a result of sublimation of TCNE from the crystal. Intensity and unit cell parameters were determined using an Enraf-Nonius CAD4 automated diffractometer. Unit cell dimensions were obtained via a least-squares refinement of 25 reflections measured between $14° < 2\theta < 27°$. Crystallographic parameters: $a = 7.273$ (2) Å, $b = 6.129$ (1) Å, $c = 22.942$ (5) Å, $\beta = 95.76$ (2)°, $Z = 4$, $V = 1017.5$ Å^3, monoclinic space group $P2_1/n$, $D_{calc} = 1.382$, $\mu = 0.78$ cm^{-1}. Intensity data were collected in the $\omega - \theta$ scan mode ($2° \leq 2\theta \leq 50°$) with a variable scan rate of 2.3–5.5° min^{-1} using graphite-monochromated Mo Kα radiation. A total of 1979 independent reflections were measured, of which 1213 were considered to be statistically significant based on the criterion $I \geq 1.0\sigma(I)$. Lorentz and polarization corrections were made, and a ψ scan based absorption correction (transmission factors 0.956–0.998) and a decay correction were applied. The structure was solved by MULTAN[8] and refined by full-matrix least-squares methods based on F with weights $w = \sigma^{-2}(F_o)$.

The asymmetric unit is comprised of one TCNE and one half-weighted carbazole, the latter disordered centrosymmetrically about the origin. The carbon and nitrogen atoms within the TCNE were refined anisotropically as was N9 in the carbazole ring. Extensive overlap between the carbon atoms reported and the centrosymmetrically generated carbon atoms in the carbazole ring, however, precluded the use of anisotropic thermal parameters in their refinement. Hydrogens H_1, H_4, H_5, and H_9 were located by difference Fourier techniques, and the other hydrogens were generated at chemically reasonable positions. The structure refined to final $R = 0.067$ and $R_w = 0.058$ with 149 parameters, $S = 0.012$ and $(\Delta/\sigma)_{max} = 0.01$. The final difference Fourier map was featureless with largest peak 0.32 e Å^{-3} in the vicinity of carbazole. Positional parameters are reported in Table I. Atomic scattering factors and anomalous dispersion corrections were taken from ref 9.

Table I. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*,[a] Å^2
C1	0.1460 (9)	0.312 (1)	−0.0672 (3)	5.8 (2)*
C2	0.1226 (8)	0.238 (1)	−0.1228 (3)	4.5 (1)*
C3	0.0426 (7)	0.0430 (8)	−0.1369 (2)	2.8 (1)*
C4	−0.0227 (6)	−0.0984 (8)	−0.0964 (2)	2.65 (9)*
C4a	−0.0017 (6)	−0.0208 (8)	−0.0371 (2)	2.7 (1)*
C4b	−0.0477 (7)	−0.1011 (8)	0.0166 (2)	3.3 (1)*
C5	−0.1338 (7)	−0.2978 (8)	0.0350 (2)	3.0 (1)*
C6	−0.1543 (7)	−0.3240 (8)	0.0924 (2)	3.0 (1)*
C7	−0.0991 (8)	−0.1773 (9)	0.1362 (3)	4.5 (1)*
C8	−0.0139 (8)	0.017 (1)	0.1211 (3)	4.6 (1)*
C8a	0.0116 (7)	0.0496 (8)	0.0625 (2)	3.2 (1)*
C9a	0.0807 (6)	0.1797 (8)	−0.0256 (2)	2.54 (9)*
N9	0.0917 (6)	0.2190 (7)	0.0346 (2)	4.7 (1)
CT1	0.5202 (3)	−0.0454 (4)	−0.1803 (1)	3.42 (6)
CT2	0.5360 (3)	0.0279 (4)	−0.1251 (1)	3.60 (6)
CT3	0.5954 (4)	0.0752 (4)	−0.2260 (1)	3.67 (6)
CT4	0.4269 (4)	−0.2474 (5)	−0.1966 (1)	3.70 (6)
CT5	0.6176 (4)	0.2377 (4)	−0.1110 (1)	3.82 (6)
CT6	0.4706 (3)	−0.0993 (4)	−0.0789 (1)	3.43 (6)
NT3	0.6564 (3)	0.1639 (4)	−0.2624 (1)	5.47 (7)
NT4	0.3519 (3)	−0.4018 (4)	−0.2111 (1)	5.23 (6)
NT5	0.6769 (3)	0.4043 (4)	−0.1007 (1)	5.00 (6)
NT6	0.4244 (3)	−0.2003 (4)	−0.0418 (1)	4.91 (6)
H1	0.209	0.459	−0.055	
H2	0.171	0.331	−0.156	
H3	0.028	−0.002	−0.180	
H4	−0.082	−0.250	−0.109	
H5	−0.209	−0.375	0.000	
H6	−0.219	−0.472	0.105	
H7	−0.121	−0.209	0.177	
H8	0.023	0.128	0.150	
H9	0.166	0.375	0.055	

[a] (*) Refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

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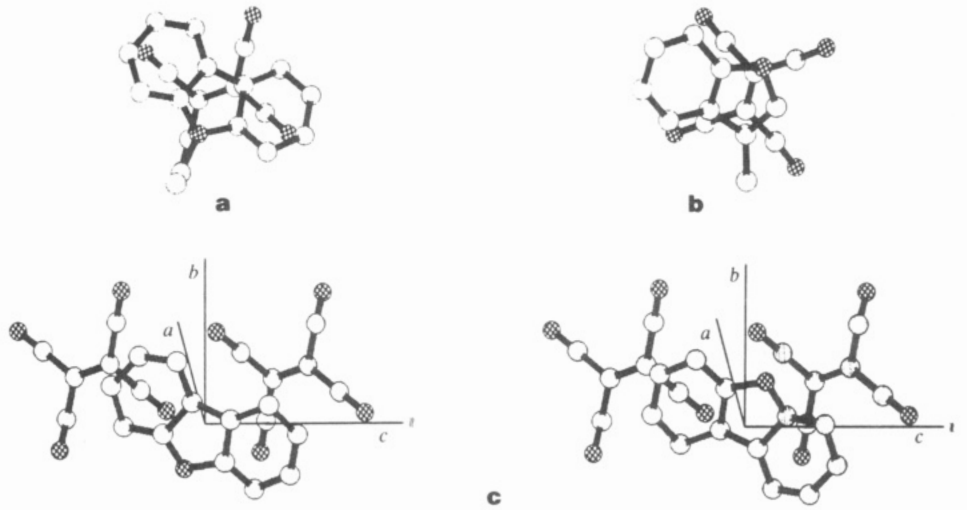

Figure 1. Molecular structures of (a) 9-ethylcarbazole–TCNE 2:1 complex (coordinates for preferred conformation from ref 13), (b) skatole–TCNE 1:1 complex (coordinates from ref 14), and (c) carbazole–TCNE 1:2 complex, all shown in a perspective perpendicular to the molecular planes. Carbons are shaded and nitrogens checkered. The two orientations of the centrosymmetrically disordered carbazole shown in c are equally populated.

Results and Discussion

A number of complexes involving weak donors such as carbazole and unsaturated acceptors such as TCNE are known.[10] Stabilization in such complexes is attributed to intermolecular interactions of the π systems.[11] According to the overlap and orientation principle developed by Mulliken,[12] the donor and acceptor molecules adopt a relative orientation which maximizes overlap between the orbitals of the donor and the acceptor principally involved in transfer of charge.

All of the electron donor–acceptor complexes between aromatic hydrocarbons and TCNE which have been characterized previously support the concept of maximization of π overlap between donor and TCNE.[13-15] The aromatic donors and TCNE generally lie in parallel planes with relative orientations which promote overlap of the HOMO of the donor with the LUMO of TCNE.[15] For example, 9-ethylcarbazole crystallizes as a 2:1 complex with TCNE.[13] The TCNE in this complex is sandwiched between two centrosymmetrically related ethylcarbazole molecules, allowing good π overlap with the central rings of both of the adjacent ethylcarbazole molecules (Figure 1a). Similarly, good overlap has been found in the crystalline 1:1 complex of skatole and TCNE, in which the donor and acceptor molecules stack alternately[14] (Figure 1b). Specifically, the highest energy donor orbitals of aromatic amines have largest coefficients on the nitrogen atoms,[16] and close contact is observed between complexed TCNE and the aromatic nitrogen of skatole or ethylcarbazole.

Table II. Bond Distances and Bond Angles in Carbazole and TCNE Structures

	carbazole–2(TCNE)[b]	carbazole[c] and TCNE[d]	2(ethylcarbazole)–TCNE[e]	dicarbazolylmethane[f]
	Bond Distance, Average,[a] Å			
C1–C2	1.376	1.374	1.369	1.38
C2–C3	1.366	1.394	1.383	1.41
C3–C4	1.368	1.392	1.366	1.37
C4–C4a	1.438	1.391	1.385	1.39
C4a–C9a	1.408	1.408	1.403	1.412
C9a–C1	1.380	1.404	1.384	1.38
C9a–N9	1.388	1.394	1.373	1.396
C4a–C4b	1.399	1.479	1.426	1.43
CT1═CT2	1.338	1.344	1.344[g]	–
CT2–CT5	1.438	1.437	1.428[g]	–
CT5≡NT5	1.126	1.135	1.130[g]	–
	Angles, Average,[a] deg			
C9a–C1–C2	117.0	115.6	117.3	117.5
C1–C2–C3	120.4	123.9	121.9	120.5
C2–C3–C4	124.8	120.1	121.0	121
C3–C4–C4a	116.7	117.9	118.5	119.5
C4–C4a–C9a	117.1	120.6	119.2	118.5
C9a–C4a–C4b	108.1	106.1	106.6	107.6
C4–C4a–C4b	134.8	133.3	133.7	133.8
C1–C9a–C4a	124.2	121.9	121.5	122.5
N9–C9a–C4a	106.8	109.7	109.1	107.5
C1–C9a–N9	129.0	128.4	129.4	130
C8a–N9–C9a	110.2	108.4	108.4	109.6
CT1═CT2–CT5	121.0	122.2	121.8[g]	–
CT5–CT2–CT6	117.9	115.6	116.0[g]	–
CT2–CT5≡NT5	177.9	178.2	172.8[g]	–

[a] Average of values for equivalent positions assuming C_{2v} symmetry for carbazole and D_{2h} symmetry for TCNE. Atomic designations of carbazole and TCNE consistent with atom designations in Figure 2. [b] This paper. [c] Structure of P_{nma} carbazole (C_{2v}) from ref 18. [d] Structure of cubic TCNE (D_{2h}) from ref 17. [e] Structure of ethylcarbazole–TCNE 2:1 complex from ref 13. [f] Structure of dicarbazolylmethane from ref 3. [g] Values weighted average for disordered TCNE, 60% orientation A and 40% orientation B.

The structure of the carbazole–TCNE 1:2 complex is noteworthy in several respects. Two essentially coplanar molecules of TCNE stack alternately with carbazole molecules. This represents the first crystalline complex observed to have a composition involving two molecules

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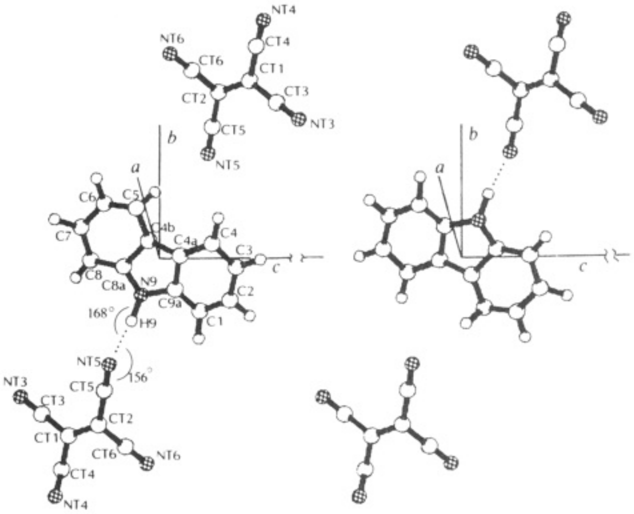
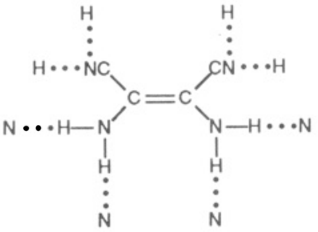


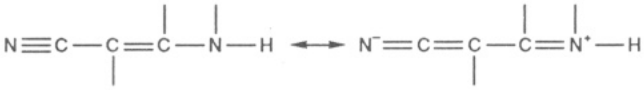
Figure 2. Structure of the carbazole–TCNE 1:2 complex showing hydrogen bonding.

of TCNE for each donor molecule. More usual are stoichiometries involving one molecule of TCNE for each donor unit or for each two donor units.[13-15] It has been found generally for donors and acceptors that form weak electron donor–acceptor complexes that the structures of the donors and acceptors are essentially the same in the complexes as in their uncomplexed forms.[13-15] Bond distances and angles found for TCNE in the carbazole–TCNE 1:2 complex are comparable to those found in uncomplexed forms of TCNE.[17] Some of the bond distances and angles of the carbazole in the complex were found to deviate slightly from the values found for uncomplexed carbazole.[18] However, these differences are undoubtedly a direct result of the disorder associated with the carbazole molecule in the structure. Average values for bond distances and angles are reported in Table II.

Importantly, there is no appreciable overlap of TCNE with the nitrogen (N9) of carbazole in the carbazole–TCNE 1:2 complex; intermolecular interactions are limited to the outer rings of carbazole (Figure 1c). π interactions in this complex are much less extensive than those in related complexes (Figure 1). Examination of intermolecular distances reveals, additionally, a close contact involving the amino hydrogen (H9) of carbazole and a nitrile nitrogen (NT5) of one TCNE (Figure 2). This interaction exists in either (equivalent) orientation of the carbazole (Figure 2). This short H···N distance and nearly linear geometry N—H···N≡C indicate the existence of a hydrogen bond[19] between H9 and the lone electron pair of NT5.

It is interesting to compare the hydrogen bond in the carbazole–TCNE 1:2 complex with the hydrogen bonds reported in related structures.[5-7] Due to the relatively low Brønsted basicity of nitriles and the low acidity of amines,[20] hydrogen bonds would be expected to be relatively weak in this kind of system. Thus, the hydrogen bonds formed between amines and nitriles typically are found to involve relatively acidic hydrogens and relatively basic nitriles of the same molecular species. For example, each molecule of crystalline diaminomalononitrile participates in eight intermolecular hydrogen bonds, one involving each hydrogen and two involving each nitrogen in a bifurcated structure (N–H···N angles 166 and 154° and N···N distances 3.16 and 3.12 Å).[5] Conjugation in such enaminonitriles should be conducive to hydrogen bond formation, due to development of partial negative charge on the cyano group and partial positive charge on the amino group.





$$N{\equiv}C{-}\underset{|}{C}{=}\overset{|}{C}{-}\overset{|}{N}{-}H \longleftrightarrow N^{-}{=}C{=}\underset{|}{C}{-}\overset{|}{C}{=}\overset{|}{N^{+}}{-}H$$

In this respect, hydrogen bond formation should be favored in cyanamide ($NCNH_2$) due to the charge disposition of the molecule (cyanamide is a weak acid[7]). Therefore, this molecule serves for comparison as a system in which the N—H···N≡C hydrogen bonds should be relatively strong. Each nitrile of cyanamide forms two hydrogen bonds to two amide hydrogens of two adjacent cyanamide molecules.[7] For one of the hydrogen bonds, angles (amide) N–H···N (nitrile) of 171° and H···N≡C of 148°, and (amide) N–N (nitrile) nonbonded distance 3.01 Å, are determined from the reported positional parameters. These values are comparable to those observed in the carbazole–TCNE 1:2 complex, which has (amine) N–H···N (nitrile) and H···N≡C angles of 168 and 156°, respectively, and an (amine) N–N (nitrile) nonbonded distance of 3.15 Å. The second hydrogen bond in cyanamide has significantly smaller angles: (amide) N–H···N (nitrile) of 155° and H···N≡C of 124°.[21]

Although TCNE has been found to serve as a Lewis base in coordination to transition metals,[22] TCNE is expected to be a very poor Brønsted base. Carbazole, however, is considerably more acidic ($pK_a = 19.9$)[23] than typical amines. This may provide the thermodynamic favorability for formation of the hydrogen bond involving carbazole. Indeed, spectroscopic studies of carbazole in solution and in the gas phase have revealed that carbazole may form a hydrogen bond with alkyl nitriles, and that interaction strengths in these hydrogen-bonded complexes in the gas phase are similar to those in electrostatic complexes.[24,25] It is apparent that hydrogen bond formation, together with electrostatic and crystallographic packing forces, dictate the atypical geometry and stoichiometry of the crystalline carbazole–TCNE 1:2 complex.

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Registry No. Carbazole–TCNE (1:2 complex), 130296-34-3.

Supplementary Material Available: Tables of bond distances, bond angles, and refined temperature factor expressions for carbazole–TCNE 1:2 complex (3 pages); table of structure factors (5 pages). Ordering information is given on any current masthead page.

Thermodynamic Basicity vs Kinetic Basicity of Diazoles (Imidazoles and Pyrazoles)

Lin-Zhi Chen, Robert Flammang,* and André Maquestiau

Université de l'Etat à Mons, Laboratoire de Chimie Organique, Faculté des Sciences, 19, Avenue Maistriau, 7000 Mons, Belgium

Robert W. Taft

Department of Chemistry, University of California at Irvine, Irvine, California 92717

Javier Catalán

Departamento de Química Física Aplicada, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

Pilar Cabildo, Rosa M. Claramunt, and José Elguero

Departamento de Química Orgánica e Instituto de Química Médica, UNED y CSIC, Ciudad Universitaria, 28040 Madrid, Spain

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The intrinsic basicity of 24 azoles (pyrazoles, indazoles, imidazoles, benzimidazoles) and 7-methylazaindole was determined by mass spectrometry techniques, ion cyclotron resonance (ICR) and/or chemical ionization (CI) in conjunction with tandem mass spectrometry (MS/MS). A reasonably good agreement ($r^2 = 0.967$) is found between both methods (15 compounds). Thus, it is possible to use CI/MS/MS to determine the intrinsic basicity of compounds not measurable by ICR for purity or volatility reasons. Some anomalies are interpreted in terms of entropy and steric effects. The basicity data are also discussed by using empirical models (σ_α, σ_R) and chelation and annelation effects.

Introduction

In the study of the intrinsic basicity of azoles, we have used both ion-cyclotron-resonance (ICR) spectrometry[1-3] and chemical ionization (CI) mass spectrometry.[4,5] These techniques analyze processes (1) and (2) respectively:

$$B + B_0H^+ \rightleftarrows BH^+ + B_0 \qquad (1)$$

$$[B_0HB^+]^* \rightarrow B_0 + HB^+ \text{ (or } B + HB_0^+) \qquad (2)$$

Both processes measure the relative basicity between B_0 and B bases. However, the first one is an equilibrium and, consequently, depends only on the energies of reagents and products, whereas the second one corresponds to the breaking of a hydrogen bond. This kinetic process will depend on the potential energy curve connecting the complex $[B_0HB^+]^*$ to its fragments. Consequently, while the firts one (1) is, in general, insensitive to steric effects,[6] the second one (2) seems to be sensitive to these effects.[7] It is the aim of this paper to compare these methods using an homogeneous set (pyridine-like nitrogen basic center, five-membered rings) of 25 compounds, most of them pyrazoles, imidazoles, and their benzo derivatives; 19 compounds were studied by ICR, 21 by chemical ionization, and 15 by both methods. Chart I contains the 25 structures.

Cooks, the discoverer of the mass spectrometric kinetic method,[8] discusses its advantages over the equilibrium method, which is hardly efficient in several circumstances (low volatility of the samples for instance).[9] In the present case, for 1*H*-benzimidazole (**11**), only an approximate value can be obtained by ICR (about 13 kcal mol^{-1} more basic than pyrazole) and the proton affinity of 1-*n*-butyl-1*H*-imidazole (**14**), 1-*tert*-butyl-1*H*-imidazole (**15**), and 1-(adamant-1-yl)-1*H*-imidazole (**20**) cannot be measured by ICR since the R^+ ion cleaves off.

Experimental Section

The synthesis of the compounds can be found in the following references: 1*H*-pyrazole (**1**) (commercial), 1*H*-indazole (**2**) (com-

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