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Synthesis, Electrochemistry, and Crystal Structure of *N,N'*-Dicyanoquinonediimine (DCNQI) Derivatives Containing Fused Benzene Rings

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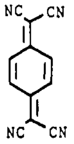
A series of novel fused aromatic *N,N'*-dicyanoquinonediimines (DCNQI) derivatives (**3**, **5**, **7**, and **9**) and *N*-cyanoquinonemonoimines (**4**, **6**, **8**, and **10**) has been synthesized by reaction of the corresponding quinones with bis(trimethylsilyl)carbodiimide (BTC). The acceptor ability is discussed in terms of both steric and electronic effects. Cyclic voltammetric data reveal two one-electron reduction waves of the corresponding radical-anion and dianion of each compound. The first reduction potentials are more negative than those of the more simple DCNQI (**2a**) and TMDCNQI (**2b**) acceptors. In contrast, the novel hybrid acceptor molecule **13** shows a single two-electron wave which corresponds to the dianion. The X-ray analysis of acceptor **13** allows one to compare, for the first time, the structural effect of the dicyanomethylene and *N*-cyanimine groups on the same molecule.

Introduction

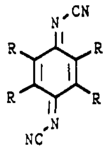
The design and synthesis of novel acceptor molecules that can form charge-transfer complexes (CTC) with donor molecules, have focused mainly on the strong acceptor tetracyano-*p*-quinodimethane (TCNQ, 1) and a wide variety of its derivatives.[1] In general, the acceptor ability of the benzene-fused TCNQ derivatives does not exceed that of TCNQ itself.[2] Some TCNQ derivatives containing fused aromatic rings[3–5] afforded highly distorted molecular structures resulting from the steric hindrance of the cyano groups and the peri-hydrogens of the fused benzene rings. The planarity of the donor and acceptor molecules has been suggested to be one of the most important requisites in the search for organic conductors.[6]

The most recently identified type of molecule with a rather planar structure and good acceptor ability is the new class of *N,N'*-dicyanoquinonediimine derivatives, e.g., DCNQI, **2**, which has been developed by Hünig and coworkers.[7] Several CT-complexes and radical anion salts containing DCNQI acceptors have been obtained recently, some of which exhibit high electrical conductivity.[8] Thus, the copper salts of various 2,5-disubstituted DCNQI do not show phase transitions into a semiconducting state even on cooling to 0.3 K.[9]

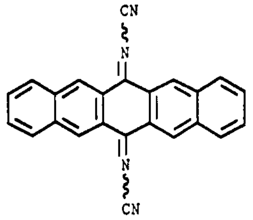
Former results by Hünig and co-workers[6] showed that only steric effects are responsible for the decrease in the first reduction potentials with increase in benzannelation in the following series: benzo > naphtho > anthraquinone derivatives. On the other hand, theoretical calculations showed that extension of the π system results in a reduction of the Coulombic repulsion in the dianion.[10] This fact, together with the better planarity of DCNQI derivatives, prompts us to synthesize (from the corresponding quinones and bis(trimetylsilyl)carbodiimide (BTC)[11]), a series of carbocyclic DCNQI derivatives **3**–**8** in which the π system has been extended systematically in order to correlate the degree of conjugation with the acceptor ability of these molecules. To the best of our knowledge, these molecules present the highest degree of conjugation for known DCNQI derivatives.



TCNQ (1)



DCNQI (2) a: R = H b: R = CH_3



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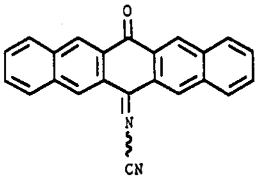

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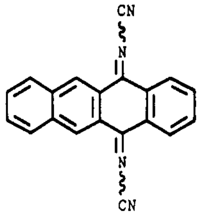

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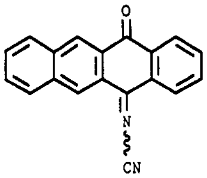

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The synthesis has been extended to the cyanimine derivatives **9** and **10** from the bianthrone and benz[*a*]-

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Table I. Yield and Spectral Data of Products

product	yield (%)	mp (°C)	molecular formula	IR (ν cm^{-1})	^{1}H-NMR (ppm) (CDCl$_3$)	MS (m/z)
3	23	>250	$C_{24}H_{12}N_4$	2175, 1599, 1548, 1262	7.70–7.86 (m, 4 H), 8.06–8.27 (m, 4 H), 9.10–9.79 (br, 4 H)	356 (M$^+$)
4	15	240 dec	$C_{23}H_{12}N_2O$	2153, 1670, 1620, 1542	7.75–7.86 (m, 4 H), 8.05–8.27 (m, 4 H), 9.0 (m, 2 H), 9.28–9.64 (br, 2 H)	332 (M$^+$)
5	20	>250	$C_{20}H_{10}N_4$	2173, 1602, 1555, 1298	7.67–7.95 (m, 4 H), 8.10–8.24 (m, 2 H), 8.51–9.10 (br, 2 H), 9.15–9.85 (br, 2 H)	306 (M$^+$)
6	19	218–219	$C_{19}H_{10}N_2O$	2158, 1670, 1560, 1299	7.69–7.82 (m, 2 H), 7.82–7.91 (m, 2 H), 8.07–8.22 (m, 3 H), 8.39–8.53 (m, 1 H), 8.92 (m, 1 H), 9.42–9.80 (br, 1 H)	282 (M$^+$)
7	28[a]	>250 dec	$C_{20}H_{10}N_4$	2165, 1597, 1568, 1559, 1292	7.70–7.82 (m, 2 H), 7.84–8.02 (m, 2 H), 8.16–8.25 (m, 1 H), 8.30–8.40 (br, 1 H), 8.72–8.78 (br, 1 H), 8.86–9.08 (br, 2 H)	306 (M$^+$)
8	14	200–201	$C_{19}H_{10}N_2O$	2152, 1668, 1587, 1278	7.73–7.83 (m, 2 H), 7.84–8.00 (m, 2 H), 8.16–8.21 (m, 1 H), 8.32–8.40 (br, 2 H), 8.71–8.78 (m, 2 H), 8.90–9.12 (br, 1 H)	282 (M$^+$)
9	9	>250	$C_{30}H_{16}N_4$	2163, 1602, 1554, 1280		432 (M$^+$)
10	15	291–293	$C_{18}H_{10}N_2$	2150, 1570, 1530, 1315	7.54 (m, 1 H), 7.68–7.80 (m, 3 H), 8.01 (d, 1 H), 8.25 (d, 1 H), 8.32 (d, 1 H), 8.47 (d, 1 H), 8.81 (br, 1 H), 9.50 (br, 1 H)	254 (M$^+$)
13	46	299–301	$C_{22}H_{10}N_4$	2226, 2169, 1600, 1573, 1543	7.69–7.82 (m, 4 H), 7.98 (m, 1 H), 8.22 (bs, 2 H), 8.29–8.32 (m, 1 H), 8.64 (br, 1 H), 9.05 (br, 1 H)	330 (M$^+$)

[a] This compound was obtained in 68% yield as the only product if the intermediate N-cyanimine is exhausted.

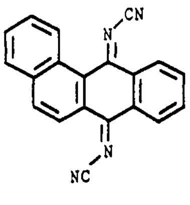
anthracene-7,12-dione. We have also prepared the little known hybrid acceptor molecules[12] in which the dicyanomethylene and cyanimine groups are present in the same molecular structure **13** and have carried out the crystallographic analysis by X-ray diffraction of this new type of hybrid molecule. The electrochemical properties of these novel compounds have been measured by cyclic voltammetry and compared with the reference parent compound, DCNQI (**2**).

Results and Discussion

The synthesis of the novel carbocyclic DCNQI derivatives has been carried out by the reaction of bis(trimethylsilyl)carbodiimide (BTC) with the corresponding starting quinones, following the previously described procedure.[7,13] Thus, the reaction of 6,13-pentacenedione, 5,12-naphthacenedione or benz[*a*]anthracene-7,12-dione with BTC, in dichloromethane solution, led to the corresponding *N,N'*-dicyanimine derivatives (**3**, **5**, and **7**) in moderate yields, together with the monocondensation compounds (*N*-cyanimine derivatives **4**, **6**, and **8**), in low to moderate yields.

The reaction can be directed to the formation of the *N,N'*-dicyanimine by heating the reaction mixture until the intermediate *N*-cyanimine is exhausted (by TLC). Thus, *N,N'*-dicyanimine **7** was obtained in 68% yield as the only reaction product.

Chart I



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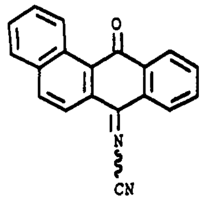

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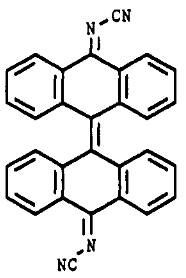

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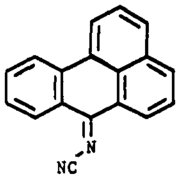

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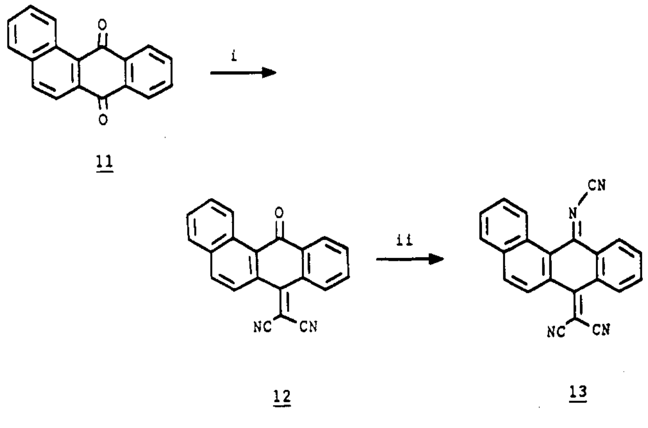
Scheme I[a]



[a] Key: (i) $CH_2(CN)_2$, $TiCl_4$, pyridine, CH_2Cl_2; (ii) BTC, $TiCl_4$, CH_2Cl_2.

Compound **9** was obtained in low yield, together with the corresponding monocyanimine derivative. The isola-

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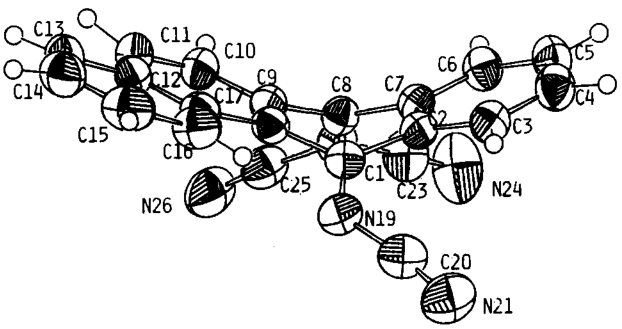

Figure 1. An ORTEP view of the molecular structure of **13**, showing the atomic numbering.

Table II. Cyclic Voltammetry Data[a] of *N*-Cyanodiimine Derivatives

compd	$E^1_{1/2red}$[b] (V)	$E^2_{1/2red}$[b] (V)	ΔE (V)	log K
2a	+0.08	−0.43	0.51	8.79
	+0.23[c]	−0.43[c]		
2b	+0.01	−0.44	0.45	7.75
3	−0.43	−0.67	0.24	4.13
5	−0.32	−0.62	0.30	5.17
7	−0.21	−0.48	0.27	4.65
	−0.05[c]	−0.46[c]		
9[d]				
10	−0.77			
13	−0.27			
	−0.21[c]			

[a] In CH_2Cl_2–0.1 M *n*-Bu_4NClO_4, containing 1 mM substrate, on glassy carbon disk. Sweep rate: 100 mV/s. [b] Potentials are quoted vs Ag/AgCl reference electrode. [c] In DMF–0.1 M *n*-Bu_4ClO_4, containing 1 mM substrate, on glassy carbon disk. Sweep rate: 100 mV/s. [d] Scarcely soluble in usual organic solvents.

tion of **9** in a pure form from the crude mixture was difficult.

The stretching vibration of the conjugated cyano groups in the IR spectra of compounds **4**, **6**, and **8** were observed at smaller wavenumbers than that of compounds **3**, **5**, and **7** (see Table I).

The synthesis of the hybrid compound **13** was carried out by reaction of benz[*a*]anthracene-7,12-dione (**11**) with malononitrile by using Lehnert's reagent[14] ($TiCl_4$ in pyridine) to yield 10-(dicyanomethylene)benz[*a*]anthrone (**12**).[5] The steric hindrance of the peri-hydrogens close to the carbonyl group prevents the second condensation. The subsequent reaction of **12** with BTC led to the formation of the tricyano derivative **13** (in a moderate yield) as stable orange crystals with a high melting point (Scheme I).

The structure of compound **13** was unambiguously determined by X-ray analysis. The molecular structure is shown in Figure 1, together with the atomic numbering scheme. The main geometrical features of the compound are collected in Table II.

All bond distances and angles within the fused ring system are in the range of values found in the literature[15] for analogous molecules, except for those involved in the ring linking the phenyl ring and the naphthalene moiety, which seem to be longer. This fact might be due to the steric hindrance and the electronic effect of the substituents attached to C1 and C8. All the angles within the C–C–N system are somewhat distorted (see Table II), due to the proximity of N26, N24, and N21 to H10, H6, and H3, respectively [2.90 (3) Å, 174.0 (3)°; 2.84 (3) Å, 175.9 (2)°; 2.81 (3) Å, 170.6 (3)°], the torsion angles on C1–N19 and on C8–C22 are quite small due to their double bond character.

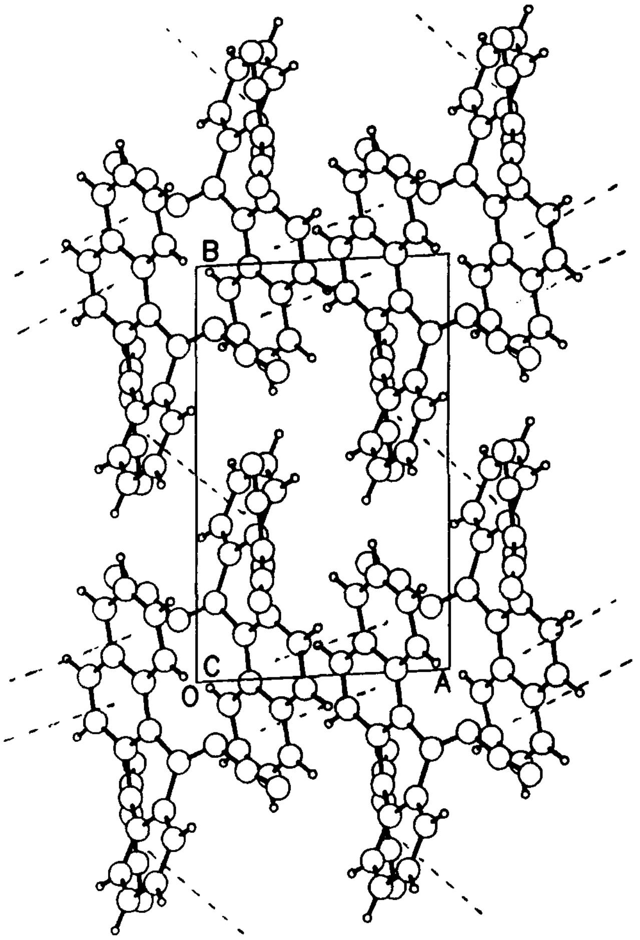

Figure 2. The crystal packing of **13**, as projected along the *c* axis, showing the intermolecular interactions.

The molecule shows a butterfly shape centered at the two substituted C-atoms, with an interplanar angle of 37.43 (4)° between the moieties. The quinoid ring presents a boat conformation. The deviation of the plane of the molecule can be described, firstly in terms of the angles between the central plane, C2–C7–C9–C18, and the external ones, C2–C3–C4–C5–C6–C7 (19.2 (1)°) and C9–C10–C11–C12–C13–C14–C15–C16–C17–C18 (19.5 (1)°); and, secondly, in terms of the angle of the central plane with those that involve the dicyanomethylene group, C7–C8–C9–C22 (32.8 (1)°) and the cyanimino group C2–C1–C18–N19 (27.5 (1)°). The planarity of the other three rings is somehow distorted in C5, 0.016 (2) Å with respect to the mean squares plane. This geometrical feature reveals a considerably more planar molecule than the corresponding bis(dicyanomethylene) derivative.[16]

Although the =NCN groups in the *N,N'*-dicyanimines obtained may occupy syn and anti positions,[7] the presence of the benzene ring close to the cyano group in compound **13** gives rise only to the structure shown in Figure 1, avoiding the steric hindrance and preserving the planarity of the molecule.

The crystal packing (Figure 2) presents a complex system of chains on the a,b plane involving aromatic inter-

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molecular interactions with an interplanar angle of around 0° and a good offset between centroids of 1.2 Å.[17,18] This overlap and the planarity of the three rings in the molecule may indicate that from a geometrical standpoint, the compound could be a good candidate as an acceptor in charge transfer complexes.

Electrochemistry

The cyclic voltammetry (CV) measurements of the above-mentioned novel compounds have been carried out in dichloromethane at room temperature, using tetrabuthylammonium perchlorate as the supporting electrolyte. Compound **9** appeared to be scarcely soluble in common organic solvents, and no CV data are available for it. All *N,N′*-dicyanoimino derivatives exhibited two one-electron reversible reduction waves, corresponding to the anion-radicals and dianions.

The increase of benzannulation in compounds **5** and **3** results in a shift of their first reduction potentials toward more negative values (Table II). A similar trend was observed within a series of derivatives of benzoquinone, naphthoquinone, and anthraquinone and has been explained by steric factors exclusively.[19] However, in the case of compounds **5** and **3** the cyanoimine groups are hindered similarly. Moreover, the angularly condensed and more strained derivative **7** reduces easier than the linearly condensed isomer **5**.

It is known that the thermodynamic stability of an anion-radical can be determined[22] from the difference in potentials of the corresponding anion-radical and dianion, using the equation $\mathrm{DE} = E^2_{\mathrm{red}} - E^1_{\mathrm{red}} = 0.059 \log K$, where K is the disproportionation constant in the equilibrium:

$$2\mathrm{A}^- \xrightleftharpoons{K} \mathrm{A} + \mathrm{A}^{2-}$$

As expected, the increase of benzannulation of dicyanoimine derivatives leads to a decrease in K: $\log K$ = 10.75, 9.13, and 5.97 for benzo-, naphtho- and anthracene derivatives, respectively,[19] and, in this work, 5.17 for **5** (tetracene derivative) and 4.13 for **3** (pentacene derivative). Apparently, such a trend in this series cannot be explained by steric factors exclusively,[19] but can be explained by taking into account the decrease in coulombic repulsion as the degree of conjugation extends.

The degree of charge delocalization as well as steric hindrance in anion-radicals increases in the following order: quinones < dicyanoimines < tetracyanomethylene derivatives, and thermodynamic stability of the anion-radicals diminishes (due to a decrease in coulombic repulsion) in the same order. The characteristic feature of the least stable anion-radical is represented by the observation that the first and second reduction waves coalescence into a single two-electron reduction wave. Indeed, tetracyanoanthraquinodimethane and higher annelated homologues exhibit only a single two-electron reduction wave.[16,19] In keeping with this observation, the hybrid compound **13** affords a single two-electron reduction wave similar to the bis(dicyanomethylene) derivative.[16]

Evidently, this work shows that with increasing benzannelation both steric and electronic factors are responsible for the decrease of both the acceptor ability and thermodynamic stability of anion-radicals.

Experimental Section

Apparatus and Chemicals. Melting points were measured with a Gahlenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 398 spectrometer and FIR spectra on a Bruker IF S-48 spectrometer. ^{1}H NMR spectra were recorded with a Bruker AC 250 and Varian XL 300S spectrometers. Mass spectra were determined with a Varian MAT 711 (70 eV) spectrometer, and elemental analyses were performed on a Carlo Erba Analyzer 1104 and 1106 apparatus.

Benz[*a*]anthracene-7,12-dione, bianthrone, and benz[*g*]anthrone were commercially available. 6,13-Pentacenedione,[5] 5,12-naphthacenedione,[24] and bis(trimethylsilyl)carbodiimide (BTC)[11] were obtained according to previously reported procedures.

Cyclic voltammetry measurements were carried out under the conditions described previously,[13] employing PAR Potentiostat/Galvanostat Model 173, PAR Universal Programmer Model 175, and Yokogawa XY-recorder Model 3086.

A General Procedure for the Synthesis of *N,N′*-Dicyanoquinonediimines and *N*-Cyanoquinonimines. The appropriate quinone (1 mmol) was dissolved in CH_2Cl_2 under inert atmosphere (argon), $TiCl_4$ (3 mmol) was added dropwise, and the mixture became dark. After addition of BTC (3.5 mmol), the reaction mixture was stirred at room temperature for 24 h. Then, CH_2Cl_2 (100 mL) and ice/water (100 mL) were added and the mixture was shaken rapidly. The organic phase was separated, dried over $MgSO_4$, filtered, and concentrated. Selective crystallization afforded the final products, which were recrystallized from a CH_2Cl_2–petroleum ether mixture or chlorobenzene.

7-(Dicyanomethylene)-12-(*N*-cyanimino)-7,12-dihydrobenz[*a*]anthracene (**13**) was obtained from 10-dicyanomethylenebenz[*a*]anthrone (**12**) by following the general procedure described above.

X-ray crystallographic data for **13**: $C_{22}H_{10}N_4$, triclinic, $P1$, M_r = 330.404, a = 7.9267 (3) Å, b = 12.305 (1) Å, c = 8.8401 (5) Å, α = 102.467 (5)°, β = 109.172 (3)°, γ = 83.709 (5)°, V = 794.5 (1) Å^3, D_c = 1.38 g/cm^3, m = 6.35 cm^{-1}, Z = 2, $F(000)$ = 340, refined cell parameters were obtained from setting angles of 68 reflections. A skew prismatic orange crystal (0.23 × 0.13 × 0.13 mm) sample was used for the analysis. Data collection: Automatic four-circle diffractometer Philips PW 1100 with graphite oriented with monochromated Cu Kα radiation. The intensity data were collected using the $\sigma/2\vartheta$ scan mode between $2 < \vartheta < 65°$; two standard reflections were measured every 90 min with no intensity variation. A total of 2707 reflections were measured, and 2350 were considered as observed ($I > 2s(I)$ criterium). The data were corrected for Lorenz and Polarization effects. Structure solution and refinement: The structure was solved by direct methods using SIR88[25] and successive Fourier synthesis. H atoms were included in mixed refinement; they were located from difference Fourier synthesis. A convenient weighting scheme was applied to obtain flat dependence in $\langle w\Delta^2F\rangle$ vs $\langle F_o\rangle$ and $\langle \sin \vartheta/\lambda\rangle$.[26] Final R (Rw) value was 5.1% (7.0). Atomic scattering factors were taken from *International Tables for X-Ray Crystallography*,[27] and calculations were performed using XTAL,[28] XRAY80,[29] and PARST.[30]

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Note Added in Proof. During the referring process, the very recent and important paper by Bryce et al. (*J. Org. Chem.* **1992**, *57*, 1690) was brought to our attention. In it, novel monocyclic mixed acceptors are reported and show good reduction potentials and a basically planar structure which becomes more distorted with bulky substituents.

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Supplementary Material Available: X-ray data for **13** as well as ^{1}H NMR spectra for compounds **3–6** and microanalytical data for compounds **7–10** and **13** (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Gas-Phase Basicity of N^1,N^1-Dimethylformamidines: Substituent Polarizability and Field Effects and Comparison with Brønsted Basicity in Solution

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Gas-phase basicities (GBs) for a series of 11 N^1,N^1-dimethylformamidines (**15–25**) bearing substituents with heteroatoms and/or π-bonds linked directly to the N^2 atom or separated by a $(CH_2)_n$ group are obtained from proton transfer equilibria measurements using FT-ICR mass spectrometry. Comparison of the GBs obtained here with those reported previously for formamidines with alkyl groups (**1–14**) (*J. Org. Chem.* **1991**, *56*, 3669–3673) confirms the earlier conclusion that for all derivatives, even for compounds with a second potentially basic site in the substituent, the N^2 atom is the favored site of protonation in the gas phase. Relative GBs of formamidines **1–25** are linearly correlated to the substituent polarizability and field effects. Deviations are observed for bifunctional compounds containing the OMe and NMe_2 groups, for which the additional lone pair enhances the basicity. The sensitivity of the amidine group to the global substituent effect (polarizability, field and "two electron pairs") as compared to the amino group in amines appears to be reduced by a factor of about 1.6 because of charge delocalization. A comparison of the gas-phase substituent effects with the substituent effects in a hydroxylic solvent (95.6% ethanol–water mixture) shows that the field effect in the gas phase is twice as large as that in solution. An electron-withdrawing field effect of the cyclopropyl group is confirmed.

Introduction

Although compounds containing the amidine group are known as very strong bases,[1,2] investigations on the gas-phase basicities and substituent effects have been reported only for imidazole and its derivatives,[3-5] 1,1,3,3-tetramethylguanidine (TMG),[6] which is the strongest monofunctional organic base in the current basicity scale,[4] and a series of N^1,N^1-dimethyl-N^2-phenylformamidines ($Me_2NCH{=}N\text{-}4\text{-}C_6H_4X$, X = NO_2, CN, COMe, Br, H, Me).[7] In a previous paper[8] we have studied the gas-phase basicity of N^1,N^1-dimethyl-N^2-substituted-formamidines [FDM*R, substituent R at N^2 restricted to alkyls; Me (**1**), Et (**2**), *n*-Pr (**3**), *i*-Pr (**4**), c-C_3H_5 (**5**), *n*-Bu (**6**), *i*-Bu (**7**), *s*-Bu (**8**), *t*-Bu (**9**), *n*-C_5H_{11} (**10**), *t*-C_5H_{11} (**11**), *n*-C_6H_{13} (**12**), c-C_6H_{11} (**13**), and 1-Adam (**14**)].

In this paper we extend our study to formamidines **15–25** with R = $(CH_2)_nX$ (*n* = 0, 1, 2, 3; X = heteroatomic and/or unsaturated group) at the N^2 atom. We report also the revised GB value for the 1-adamantyl derivative

$Me_2NCH{=}NR$ (FDM*R)

15: R = OMe
16: R = NMe_2
17: R = CH_2CN
18: R = CH_2CF_3
19: R = $CH_2C{\equiv}CH$
20: R = $CH_2CH{=}CH_2$
21: R = CH_2Ph
22: R = $(CH_2)_2CN$
23: R = $(CH_2)_2OMe$
24: R = $(CH_2)_2NMe_2$
25: R = $(CH_2)_3NMe_2$

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