Reductive activation of arenes

20.* Anionic products of two-electron reduction of tolunitriles in liquid ammonia: the nature and electronic structure**

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Stable cyanomethylcyclohexadienyl anions generated in two-electron reduction of isomeric tolunitriles by potassium in liquid ammonia were detected by NMR spectroscopy. The chemical shifts in these anions were obtained from density functional (PBE/3z) quantum chemical calculations and the electron density distributions for the anions were calculated in the framework of the NBO approach at the HF/6-31+G* level of theory. The experimental and calculated δ_C values are in good agreement. Changes in the δ_C values on going from the starting nitriles to the corresponding anions are linearly related to the calculated π-electron densities on the pentadienyl ring carbon atoms.

Key words: aromatic nitriles, reduction in liquid ammonia, cyanocyclohexadienyl anions, NMR spectroscopy, quantum chemical calculations, linear correlations.

Two-electron reduction of aromatic nitriles, namely, benzonitrile (**1**), tolunitriles (*para*-, *meta*-, and *ortho*-isomers **2—4**, respectively), 1-naphthonitrile, and 9-cyanoanthracene by alkali metals in liquid ammonia or in liquid ammonia—methanol mixtures allows preparative amounts of corresponding cyanodihydroaryl anions to be generated. This was proved by chemical tests. Anions derived from nitrile **1** and some other unsubstituted arenecarbonitriles were directly detected by NMR spectroscopy.[2] These anions are produced as a result of protonation of the primary generated dianions of the starting nitriles at the carbon atom in *para*-position relative to cyano group (Scheme 1). Early studies revealed that these anions are relatively stable and highly reactive in the reactions with electrophilic reagents. This offers prospects for the generation of cyanodihydroaryl anions in preparative amounts and application of these species as reagents in organic synthesis. For instance, they react with alkyl halides to give high yields of corresponding alkylcyanodihydroarenes.[3] If electrophiles are relatively stable to NH₃, the latter can be used as a solvent that ensures high reactivity of the anionic species.[4]

Scheme 1

X = H (**1**), *p*-Me (**2**), *m*-Me (**3**), *o*-Me (**4**)
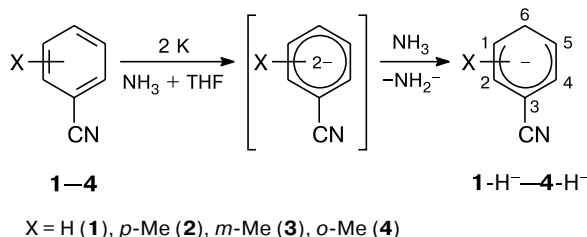
In a continuation of these investigations, here we present the results of an NMR study on the nature of methyl-substituted 3-cyanocyclohexa-1,4-dienyl anions generated in two-electron reduction of isomeric tolunitriles **2—4** by potassium in liquid ammonia. Additionally, we were interested in studying peculiar features of the electronic structure of the anions produced and in comparing the results obtained with the available data for 3-cyanocyclohexadienyl anion generated from nitrile **1**[2] and for methyl-substituted cyclohexadienyl anions containing no cyano groups.[5]

Experimental

Liquid ammonia was purified by dissolution of metallic sodium and subsequent distillation to a reaction vessel cooled

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* For Part 19, see Ref. 1.
** Dedicated to the memory of Academician V. A. Koptyug on the occasion of the 75th anniversary of his birth.

to −70 °C. THF was purified by boiling over benzophenone ketyl followed by distillation in argon atmosphere. The oxide film was removed from metallic potassium under an anhydrous hexane layer. Nitriles **1—4** were purified by distillation over P_2O_5.

Production of cyclohexadienyl anions. A Schlenk flask (volume 30 mL) attached to a NMR tube (diameter 10 mm) was filled with potassium (164 mg, 4.2 mmol), ammonia (10 mL) was condensed into the flask, and a solution of nitrile (2 mmol) in THF (5 mL) was added with stirring. Ammonia was evaporated, the flask was attached to a high-vacuum line, and THF was removed. To a dry residue, ammonia (4 mL) and THF-d_8 (0.3 mL) were condensed, the solution was transferred to the NMR tube, and the NMR tube was sealed.

Recording NMR spectra. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM-400 spectrometer at −65 °C using deuterated THF as internal reference. To ensure reliable signal assignment, broadband decoupled [13]C—{[1]H} spectra and spectra with off-resonance and selective proton irradiation were recorded.

Anion 1-H⁻. ^{1}H NMR spectrum (NH₃, THF-d_8), δ: 3.24 (s, 2 H, H(6)); 3.89 (d, 2 H, H(1), H(5)); 5.68 (d, 2 H, H(2), H(4)).

Anion 2-H⁻. ^{1}H NMR spectrum (NH₃, THF-d_8), δ: 3.28 (br.s, 1 H, H(6)); 3.91 (d, 2 H, H(1), H(5)); 5.70 (d, 2 H, H(2), H(4)); signal of Me group is strongly overlapped with an intense peak of NH₃ protons.

Anion 3-H⁻. ^{1}H NMR spectrum (NH₃, THF-d_8), δ: 1.74 (s, 3 H, Me); 3.10 (s, 2 H, H(6)); 3.88 (d, 1 H, H(5)); 5.37 (s, 1 H, H(2)); 5.69 (d, 1 H, H(4)).

Anion 4-H⁻. ^{1}H NMR spectrum (NH₃, THF-d_8), δ: 1.43 (s, 3 H, Me); 3.20 (s, 2 H, H(6)); 3.69 (s, 1 H, H(1)); 3.85 (d, 1 H, H(5)); 5.65 (d, 1 H, H(4)).

The ^{13}C NMR spectra are presented in Table 1.

Results and Discussion

The NMR spectral parameters of anions **1-H⁻—4-H⁻** derived from nitriles **1—4**, respectively (see Scheme 1), are listed in Table 1 (see also Experimental).

Earlier,[2] the spectrum of a solution obtained by the action of two equivalents of potassium on nitrile **1** exhibited signals of 3-cyanocyclohexa-1,4-dienyl anion (**1-H⁻**) and a number of signals that were not interpreted. A possible reason for the appearance of these signals consists in the presence of impurities that are formed owing to low stability of the anion or as a result of its contact with the residual oxygen and trace amounts of water. The ^{13}C NMR spectrum of the solution prepared in this work by the reaction of nitrile **1** with two equivalents of potassium in liquid ammonia exhibits a complete set of the signals of anion **1-H⁻** (see Table 1, *cf.* data in Ref. 2) and only one additional signal detected earlier (weak doublet at δ 88.1). The reduction products of nitriles **2—4** generated under identical conditions are also stable and do not show any (visible) changes on the time scale of NMR spectral data acquisition (at least 3 h).

The two-electron reduction product of nitrile **2** is 3-cyano-6-methylcyclohexa-1,4-dienyl anion (**2-H⁻**). The simplest way of interpreting the ^{13}C NMR spectrum

Table 1. ^{13}C NMR spectral parameters of 3-cyanocyclohexadienyl anions **1-H⁻—4-H⁻** obtained experimentally (δ_C^{exp}; NH₃, THF-d_8) and from DFT (PBE/3z) calculations (δ_C^{calc}), the total charge (q_t) distribution over the pentadienyl ring carbon atoms C(1)—C(5), and the π-electron charges (q_π) of the C(1)—C(5) atoms in anions **1-H⁻—4-H⁻** obtained from the NBO calculations (HF/6-31+G*)

Anion	Atom[a]	δ_C		$\Delta\delta_C$[b] $[\Sigma\Delta\delta_C]$	q_t	q_π $\{\Sigma q_\pi(CN)\}$[c]
		δ_C^{exp}	δ_C^{calc}			
1-H⁻ [d]	C(1)	97.8	98.4	−31.4	−0.375	−0.201
	C(2)	130.5	137.4	−1.6	−0.130	0.072
	C(3)	51.0	63.9	−61.4	−0.506	−0.436
	C(4)	130.5	137.4	−1.6	−0.130	0.072
	C(5)	97.8	98.4	−31.4	−0.375	−0.201
				[−127.4]		{−0.212}
2-H⁻ [e]	C(1)	103.4	102.0	−26.6	−0.371	−0.206
	C(2)	128.0	134.8	−3.9	−0.131	0.069
	C(3)	52.1	70.1	−57.4	−0.499	−0.424
	C(4)	128.0	134.8	−3.9	−0.131	0.069
	C(5)	103.4	102.0	−26.6	−0.371	−0.206
				[−118.4]		{−0.200}
3-H⁻ [f]	C(1)	104.5	102.2	−34.8	−0.168	−0.154
	C(2)	123.5	132.3	−8.8	−0.129	0.051
	C(3)	49.4	65.6	−63.9	−0.493	−0.430
	C(4)	129.3	135.5	+0.1	−0.128	0.072
	C(5)	96.4	98.3	−32.8	−0.381	−0.207
				[−139.3]		{−0.211}
4-H⁻ [g]	C(1)	96.9	97.4	−33.4	−0.375	−0.202
	C(2)	135.8	143.8	−6.0	−0.126	0.073
	C(3)	53.8	66.9	−59.1	−0.498	−0.442
	C(4)	131.3	137.5	−1.1	0.051	0.088
	C(5)	97.5	95.8	−28.9	−0.366	−0.211
				[−128.5]		{−0.214}

[a] ^{13}C NMR spectra of other C atoms are listed below.
[b] Changes in the chemical shifts on going from precursors[6] to anions; the sum of the changes for the C(1)—C(5) atoms is given in square brackets.
[c] Total π-electron charge localized on the C and N atoms of the cyano group.
[d] ^{13}C NMR (NH₃, THF-d_8), δ: 30.1 (C(6)); 139.6 (CN).
[e] ^{13}C NMR (NH₃, THF-d_8), δ: 32.5 (C(6)); 138.8 (CN); 27.9 (Me).
[f] ^{13}C NMR (NH₃, THF-d_8), δ: 30.4 (C(6)); 139.9 (CN); 22.2 (Me).
[g] ^{13}C NMR (NH₃, THF-d_8), δ: 34.9 (C(6)); 141.8 (CN); 24.9 (Me).

of the solution of **2-H⁻** is to use an analogy with the NMR spectrum of anion **1-H⁻**. The singlets at δ 52.1 and 138.8 can be assigned to the C(3) atom and the cyano carbon atom, respectively. The doublet at δ 128.0 was attributed to the C(2) and C(4) atoms. Based on the commonly accepted concepts of the π-electron charge distribution over the dienyl system, these atoms seem to be almost not involved in delocalization of this charge. The high-field doublet at δ 103.4 was assigned to the C(1) and C(5)

atoms. This signal is shifted by ~6 ppm to the low-field region relative to the corresponding signal in the spectrum of anion **1**-H⁻ owing to the effect of the Me group at the sp³-hybridized atom C(6). A similar effect of introducing a Me group at the geminal site was observed for cyanodihydronaphthyl[3] and cyclohexadienyl[5] anions. The signal assignment for the saturated carbon atom C(6) and the methyl carbon bonded to it is based on the analysis of the ¹³C NMR spectrum with off-resonance proton irradiation (perturbing field frequency was set near δ 0.0). Namely, the signal at δ 32.5 is a doublet with a residual splitting of 114 Hz and therefore should be attributed to the C(6) atom. The signal at δ 27.9 corresponds to a resonance of the methyl carbon atom. A low intensity of the signal makes only two inner components of the expected quartet visible. The residual splitting of 63 Hz is smaller than for the C(6) atom due to the frequency difference between the perturbing field and the C(6)H and CH_3 proton resonances.

The ¹³C NMR spectra of unsymmetric 3-cyano-1-methyl- (**3**-H⁻) and 3-cyano-2-methylcyclohexa-1,4-dienyl (**4**-H⁻) anions generated in the reduction of nitriles **3** and **4**, respectively, exhibit eight signals each. They include singlets of the carbon atom C(3) and the cyano carbon atom bonded to it, whose positions are similar to those of the corresponding signals in the spectra of anions **1**-H⁻ and **2**-H⁻. Singlets of the cyclohexadienyl carbon atoms bonded to the Me group (C(1) and C(2) in anions **3**-H⁻ and **4**-H⁻, respectively), are shifted by ~5—7 ppm to the low-field region relative to positions of the signals of the corresponding unsubstituted atoms in the spectrum of anion **1**-H⁻. Signals of the saturated ring carbon atoms and the methyl carbon atoms in both cases appear in the region δ ~22—35 as triplets and quartets, respectively. The doublet signals of the unsubstituted cyclohexadienyl ring C atoms were assigned taking into account the involvement of these atoms in delocalization of the negative charge over the π-electron system, the effect of the neighboring Me group, and the residual splitting in the spectra with off-resonance and selective proton irradiation. In particular, the doublet at δ 96.4 in the spectrum of anion **3**-H⁻ apparently originates from the C(5) atom; this signal experiences a characteristic highfield shift relative to the corresponding signal in the spectrum of the initial compound **3** due to the appearance of a negative charge on this atom. The doublets at δ 123.5 and 129.3 in the spectrum of anion **3**-H⁻ were attributed to the C(2) and C(4) atoms, respectively, based on the results of the double resonance experiment with selective irradiation of the H(2) proton. Note also that the signal of the C(2) atom is shifted by 7 ppm to the high-field region relative to the corresponding signal in the spectrum of unsubstituted anion **1**-H⁻ due to the effect of the neighboring Me group. This effect is also characteristic of the 1-methylcyclohexadienyl anion containing no cyano

group.[5] In the spectrum of anion **4**-H⁻ the chemical shift (δ 131.3) of the doublet signal of the C(4) atom, which is almost not involved in delocalization of the excess electron density, nearly coincides with the chemical shift of the signal of this atom in the spectrum of initial nitrile **4**. The doublets at δ 96.9 and 97.5 were assigned to the C(1) and C(5) atoms in anion **4**-H⁻, respectively, based on the magnitudes of the residual splittings in the ¹³C—{¹H} NMR spectrum with off-resonance proton irradiation at a frequency similar to the resonance frequency of the H(5) proton ($J_{C(5),H} = 49.4$ Hz, $J_{C(1),H} = 75.6$ Hz).

The signals of the cyano carbon atoms in the spectra of anions **1**-H⁻—**4**-H⁻ are shifted by +20—22 ppm to the low-field region relative to the corresponding signals in the spectra of the initial compounds. This is likely due to the change from acetylenic to allenic character of these atoms during transformations of neutral nitriles to cyanocyclohexadienyl anions owing to efficient involvement of the cyano group in delocalization of the excess electron density by the resonance mechanism (Scheme 2).

Scheme 2
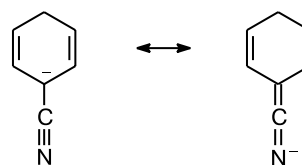
A similar explanation for this effect, based on comparison of the chemical shifts of the sp-hybridized carbon atoms in the ¹³C NMR spectra of alkynes and allenes,[7] was reported earlier for cyanodihydroaryl anions.[2]

The validity of the signal assignment for the pentadienyl ring carbon atoms in the ¹³C NMR spectra of anions **1**-H⁻—**4**-H⁻ and their analogs containing no cyano groups[5] (see above) is substantiated by the results of DFT (PBE/3z) calculations of $δ_C$ values using the PRIRODA program[8] (see Table 1). For all carbon atoms in anions **1**-H⁻—**4**-H⁻, except for the C(3) atom bonded to the cyano group, the calculated and experimental $δ_C$ values are in good agreement (correlation coefficient $r = 0.99$). The inclusion of the $δ_C$ values for the C(3) atom somewhat reduces the correlation quality ($r = 0.98$) because here the experimental and calculated δ values differ much larger (by 13—18 ppm) than for the atoms C(1), C(2), C(4), and C(5). This can be due to the fact that calculations either incorrectly allow for the induction effect of the cyano group or ignore the solvation effects. These assumptions are also substantiated by the fact that the differences between the experimental and calculated $δ_C$ values for the C(2) and C(4) atoms bonded to the C(3) atom are larger than those obtained for the distant atoms C(1) and C(5).

Table 2. Experimental and calculated characteristics of cyclo-hexadienyl anions **5—8**

An-ion	Atom	^{13}C NMR, δ		$\Delta\delta_C$*	$\Sigma\alpha$**
		δ_C^{exp} (NH$_3$)[5]	δ_C^{calc} (PBE/3z)		
5	C(1)	75.8	73.6	−52.7	359.51
	C(2)	131.8	133.4	3.3	359.80
	C(3)	78.0	88.7	−50.5	356.12
	C(4)	131.8	133.4	3.3	359.80
	C(5)	75.8	73.6	−52.7	359.51
6	C(1)	86.2	86.7	−42.0	359.73
	C(2)	129.1	130.6	0.1	359.88
	C(3)	77.5	86.8	−47.8	357.96
	C(4)	129.1	130.6	0.1	359.88
	C(5)	86.2	86.7	−42.0	359.73
7	C(1)	89.8	87.4	−48.0	358.81
	C(2)	127.8	131.7	−0.4	359.97
	C(3)	79.5	81.7	−49.5	357.43
	C(4)	131.5	133.0	6.2	359.92
	C(5)	70.7	86.8	−58.3	359.47
8	C(1)	77.7	78.0	−50.5	359.62
	C(2)	139.9	141.4	2.1	359.86
	C(3)	77.1	86.1	−51.1	355.86
	C(4)	132.6	134.2	3.1	359.77
	C(5)	77.9	75.1	−47.4	359.42

* Changes in the chemical shifts on going from precursor to anion.
** The sum of the bond angles.

The experimental[5] and DFT calculated δ_C values of the cyclohexadienyl (**5**) and isomeric 6-methyl- (**6**), 1-methyl- (**7**), and 2-methylcyclohexadienyl (**8**) anions that contain no cyano group (Table 2) and thus differ from anions **1**-H$^-$—**4**-H$^-$ are in good agreement ($r = 0.98$). At the same time, there is a trend toward a worse correspondence between the experimental and calculated δ_C values for the C(3) atom compared to other pentadienyl ring carbon atoms. Possible reasons can be associated with nonplanar configurations of the cyclohexadienyl anions **5—8** (see Table 2). By and large there is a good correlation between the calculated and experimental δ values for anions **1**-H$^-$—**4**-H$^-$ and **5—8** ($r = 0.98$).

In order to reveal specific features of the electronic structure of cyclohexadienyl anions, the experimental δ_C values for anions **1**-H$^-$—**4**-H$^-$ and **5—8** were compared with the results of the electron density distribution calculations carried out in the framework of the natural bonding orbital (NBO) scheme.[9] The Hartree—Fock (HF/6-31+G*) calculations were performed using the GAMESS[10] and NBO* programs and the geometric parameters of anions optimized by the PBE/3z method. The results obtained for anions **1**-H$^-$—**4**-H$^-$ show no

* http://www.ccl.net/cca/software/SOURCES/FORTRAN/nbo/index.shtml.

correspondence (even qualitative!) between the calculated total charge (q_t) distribution over the pentadienyl ring carbon atoms C(1)—C(5) and the δ_C values (see Table 1). Calculations predict planar configurations of the atoms C(1)—C(5) in anions **1**-H$^-$, **3**-H$^-$, and **4**-H$^-$ and a minor deviation of 0.025° of the sums of the bond angles ($\Sigma\alpha$) from 360° for anion **2**-H$^-$, which makes it possible to select the populations of the valence $\pi(2p_z)$-orbitals of these atoms. The data listed in Table 1 show that the π-electron charges (q_π) thus calculated for the C(1)—C(5) atoms in anions **1**-H$^-$—**4**-H$^-$ are in good agreement with the corresponding δ_C values. The changes in the δ_C values on going from initial nitriles to corresponding cyano-cyclohexadienyl anions ($\Delta\delta_C$) and the q_π values are related by a linear equation

$$\Delta\delta_C = 110.7q_\pi - 10.5 \ (r = 0.99).$$

The relationship established earlier[2] for a number of unsubstituted cyanocyclohexadienyl anions including **1**-H$^-$ using the q_π values obtained from semiempirical calculations has the form:

$$\Delta\delta_C = (125\pm5)q_\pi.$$

These expressions are similar and seem to correctly describe the relations between the changes in δ_C on going from neutral precursors to cyclohexadienyl anions and the π-electron charges of the anions in the absence of the out-of-plane distortions.

A comparison of the relations for δ_C for the atoms C(3) and C(1), C(5) in (i) anions **1**-H$^-$—**4**-H$^-$ and (ii) anions **5—8**[5] indicates a shift of the π-electron density in the pentadienyl system to the C(3) atom under the action of the cyano group. This is in excellent agreement with the fact that protonation and alkylation of cyano-cyclohexadienyl anions occur exclusively at the C(3) atom.[3] In contrast to this, the relations for δ_C for the atoms C(1) and C(3) in anions **5—8** are inconsistent with the corresponding protonation pathways, thus indicating[5] that the chemical shifts of the pentadienyl ring carbon atoms in these species are governed not only by the π-electron density distribution.

Based on the sums of the $2p_z$-orbital populations of the C and N atoms, the π-electron charge localized on the cyano groups in anions **1**-H$^-$—**4**-H$^-$ is of the order of −0.20 to −0.22. These values somewhat exceed those obtained earlier[2] from semiempirical calculations for anion **1**-H$^-$ and other unsubstituted cyanocyclohexadienyl anions (−0.14 to −0.17). Therefore, the *ab initio* calculations predict a π-electron charge redistribution from the pentadienyl system to the cyano group. By and large the available data suggest that the interval from −0.10 to −0.20 provides a correct estimate of the variation of the π-electron charge on the cyano group in this type of anions.

Assessment of the effect of the Me group on the total π-electron charge of the pentadienyl system based on the $\Sigma\Delta\delta_C$ values for the C(1)—C(5) atoms (see Table 1) is only possible for planar cyanocyclohexadienyl anions **1**-H⁻—**4**-H⁻. Here, the Me group introduced at the C(2) atom has almost no effect, which seems to be quite natural with allowance for the absence of excess electron density at this position. The introduction of the Me group at the C(1) and C(6) atoms respectively causes an increase and a decrease in the total π-electron charge of the pentadienyl system. Interpretation of the observed changes in the $\Sigma\Delta\delta_C$ values deserves a special study.

Thus, in this work cyanomethylcyclohexadienyl anions generated in two-electron reduction of isomeric tolunitriles by potassium in liquid ammonia were detected by NMR spectroscopy. The anions are stable under the generation conditions. We obtained good agreement between the experimental δ_C values and those found from density functional PBE/3z calculations. In order to reveal specific features of the electronic structure of cyclohexadienyl anions, the experimental δ_C values were compared with the results of the electron density distribution calculations performed in the framework of the NBO approach. For the pentadienyl carbon atoms of the anions under study we found a linear correlation between the changes in the δ_C values on going from nitriles to anions and the q_π charges. This allows one to evaluate the π-electron density distribution in this type of anions from the ¹³C NMR spectral parameters and thus to some extent predict the course of the chemical transformations initiated by the reductive activation of aromatic nitriles.

References

1. E. V. Panteleeva, T. A. Vaganova, E. A. Luk´yanets, and V. D. Shteingarts, *Zh. Org. Khim.*, 2006, **42**, 1301 [*Russ. J. Org. Chem.*, 2006, **42**, No. 9 (Engl. Transl.)].
2. I. I. Bilkis, T. A. Vaganova, E. V. Panteleeva, A. P. Tananakin, G. E. Salnikov, V. I. Mamatyuk, and V. D. Shteingarts, *J. Phys. Org. Chem.*, 1994, **7**, 153.
3. I. I. Bilkis, T. A. Vaganova, E. V. Panteleeva, A. P. Tananakin, and V. D. Shteingarts, *Tetrahedron*, 1994, **50**, 10011; I. I. Bil´kis, T. A. Vaganova, and V. D. Shteingarts, *Zh. Org. Khim.*, 1994, **30**, 892 [*Russ. J. Org. Chem.*, 1994, **30**, 951 (Engl. Transl.)]; T. A. Vaganova, E. V. Starokon´, and V. D. Shteingarts, *Zh. Org. Khim.*, 2002, **38**, 865 [*Russ. J. Org. Chem.*, 2002, **38**, 823 (Engl. Transl.)]; T. A. Vaganova, E. V. Starokon´, and V. D. Shteingarts, *Zh. Org. Khim.*, 2003, **39**, 725 [*Russ. J. Org. Chem.*, 2003, **39**, 680 (Engl. Transl.)].
4. E. V. Malykhin and V. D. Shteingarts, *Ros. Khim. Zh.*, 1999, **43**, 49 [*Mendeleev Chem. J.*, 1999, **43** (Engl. Transl.)].
5. G. A. Olah, G. Asensio, H. Mayr, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1978, **100**, 4347.
6. *Sadtler Standard Spectra, ¹³C NMR Spectra*, Sadtler Research Laboratories, Philadelphia, 1968—1978.
7. H. O. Kalinovsky, S. Berger, and S. Braun, *¹³C NMR Spectroscopy*, Wiley, New York, 1988, 147.
8. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
9. J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.*, 1980, **102**, 7211; A. E. Reed and F. Weinhold, *J. Chem. Phys.*, 1983, **78**, 4066; A. E. Reed, R. B. Weinstock, and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735.
10. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, H. Jensen, S. Koseki, N. Matsunaga, K. Su, S. Nguyen, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.