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1,8-Bis(dialkylamino)-4,5-dinitronaphthalenes and 4,5-Bis(dimethylamino)-naphthalene-1,8-dicarbaldehyde as "Push–Pull" Proton Sponges: When and Why Formyl Groups Become Stronger π-Electron Acceptors than Nitro Groups

Valery A. Ozeryanskii,*[a] Alexander F. Pozharskii,[a] Alexander K. Artaryan,[a] Nikolai V. Vistorobskii,[a] and Zoya A. Starikova[b]

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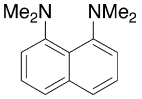
Single-crystal X-ray studies of four representatives of "push–pull" proton sponges, namely 1,8-bis(dimethylamino)-, 1,8-bis(diethylamino)-, 1,8-bis(dipropylamino)-4,5-dinitronaphthalenes and 4,5-bis(dimethylamino)naphthalene-1,8-dicarbaldehyde have been performed at low and ambient temperatures. The most interesting and unexpected result is that the formyl groups in the *peri*-dialdehyde display stronger π-acceptor effects than the nitro groups. This phenomenon is ascribed to smaller steric demands of the CHO groups, their lower electrostatic repulsion, and specific packing forces. The naphthalene cores of all but one of the molecules are markedly twisted (21–26°) while that of the diethylamino derivative is not (<5°), providing different and somewhat unpredictable ways of resonance stabilization and steric relaxation. The through-conjugation in the above compounds is also discussed for gas and solution phases on the basis of theoretical calculations, UV/Vis and ^{1}H NMR spectra.

Introduction

Organic donor–acceptor molecules with π-donor (D) and π-acceptor (A) substituents on the opposite ends of a conjugated π-system are extensively studied compounds due to their nonlinear optical[1–3] and other[2,4,5] interesting properties. A general strategy for their search consists in increasing donor–acceptor strength and overall number of groups A and D, as well as the use of more extended and polarizable π-systems. In this context, push–pull naphthalene systems can be rather attractive. Indeed, some of them were the focus of recent investigations devoted to intramolecular charge transfer processes,[6,7] designing new fluorophores,[8–10] π-extended structures,[11] and advanced synthetic methodologies.[12]

Extensive studies of 1,8-bis(dimethylamino)naphthalene (proton sponge, **1**) and its derivatives have shown that the dimethylamino groups display a rather strong π-donor effect, especially pronounced in the presence of conjugated –M-substituents in the ring (see ref.[13] for reviews). A marvellous example of such compounds is 4,5-bis(dimethylamino)naphthalene-1,8-dicarbaldehyde (**2**), which was described some time ago by two of us.[14] Unlike colourless, slightly polar (μ = 1.19 D, C_6H_6, 25 °C) and strongly hydrophobic parent compound **1**, the dialdehyde **2** is notably soluble in water and has a surprisingly high dipole moment (μ = 9.21 D), making it an almost ionic substance.[14b] The dark orange–brown colour with metallic lustre of **2** is in accord with these properties. Clearly, the NMe_2 and CHO groups in molecule **2** are strongly conjugated, which can be expressed via a large contribution of bipolar resonance structures **2b**–**2e**.



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The single-crystal X-ray structure obtained for **2** at room temperature (Figure 1)[14b] has nicely demonstrated that the effective through-conjugation in **2** is provided by 1) unprecedented enlargement of the N···N distance, 2) orientation of the aldehyde hydrogen atoms towards each other and the carbonyl oxygens outwards, and 3) considerable distortion of the naphthalene ring system compared to **1**. A torsion angle, ABCD, taken as a simple and convenient measure of ring twisting,[15] measures as much as 26° for molecule **2**, compared to 11° for **1**.[16,17] All these changes maximize planarization and mutual coplanarity of the functional groups. Notably, until now, dialdehyde **2** remains the most distorted naphthalene proton sponge derivative with the largest N···N distance (3.03 Å).[14b]

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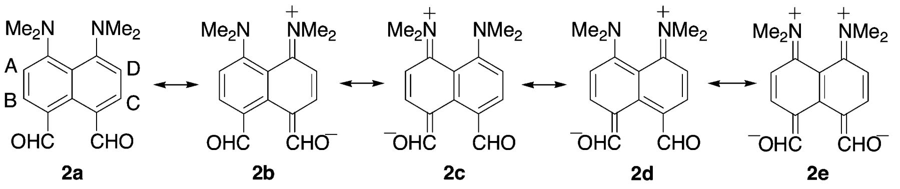
[a] Department of Organic Chemistry, Southern Federal University,
Zorge 7, 344090 Rostov-on-Don, Russian Federation
Fax: +7-863-2975146
E-mail: vv_ozer2@rsu.ru
[b] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
Vavilova 28, 119991 Moscow, Russian Federation



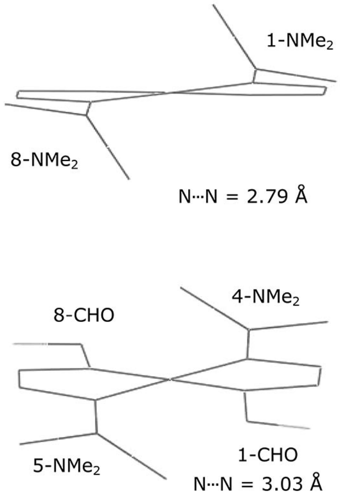
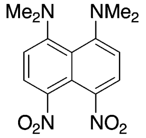


Figure 1. Orientation of functional groups with regard to the naphthalene ring system in the X-ray structures of proton sponge **1** (top) and *peri*-dialdehyde **2** (bottom) (view along the average ring plane with the amino groups directed toward the viewer).

In light of the above survey, the present work was designed to explore the structural behaviour of *peri*-dinitro analogues of **2**. We reasoned that since the NO_2 group is a much more powerful electron acceptor than the CHO group (σ_p = 0.78 and 0.22, respectively[18]), the structural and other properties of 1,8-bis(dialkylamino)-4,5-dinitronaphthalenes might be intriguing. For our studies, we chose three representatives of such compounds with *peri*-dimethylamino (**3**), diethylamino (**4**), and dipropylamino (**5**) groups. The first two were already described[19–21] but the latter one was unknown. We expected that increasing bulkiness of the $NAlk_2$ groups would cause additional molecular distortions[22] and lead to somewhat unpredictable results. We also performed variable-temperature X-ray experiments and compared the results obtained for the solid samples with that for the gas phase (DFT calculations) and solution (UV/Vis and NMR) spectroscopic data. For dialdehyde **2** we repeated X-ray measurements at room temperature and for the first time performed the experiment at 100 K.



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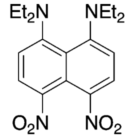

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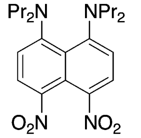

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Results and Discussion

Molecular and Crystal Structures

Crystal structures of diamines **2**–**4** are formed by one crystallographically independent molecule, $C_{16}H_{18}N_2O_2$, $C_{14}H_{16}N_4O_4$ or $C_{18}H_{24}N_4O_4$, while that of **5** is formed by two independent molecules, $C_{22}H_{32}N_4O_4$. The molecules of **3** and **5** have a twofold symmetry axis passing through the C(5) and C(6) atoms of the naphthalene cycle, while **2** and **4** are slightly different with regard to their halves (Figures 2 and 3). The terminal $–CH_2CH_3$ fragments of two of the four propyl substituents in one molecule of **5** are disordered at 120 K over two positions with probabilities equal to 0.540 and 0.460. For two compounds, namely **2** and **3**, new accurate single-crystal X-ray diffraction data including low-temperature measurements were obtained.

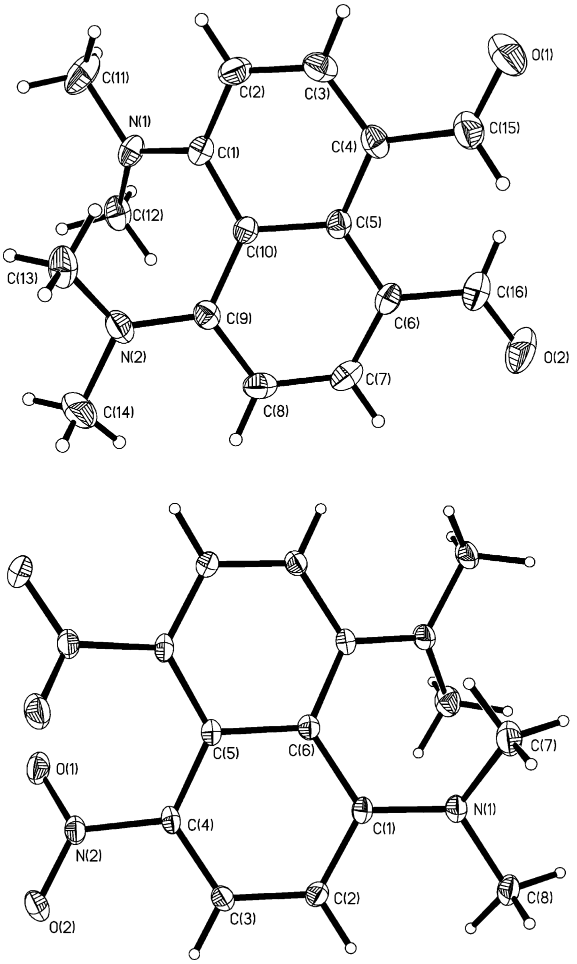


Figure 2. The molecular structures of dialdehyde **2** (top) (100 K) and dinitronaphthalene **3** (bottom) (100 K) showing thermal displacement ellipsoids (drawn at 30% probability level for non-hydrogen atoms) and the atom numbering scheme.

The results show that internal charge transfer raises steric strain in molecules **2** and **3**, mainly occurring from spatial and electrostatic repulsion between two pairs of the *peri*-

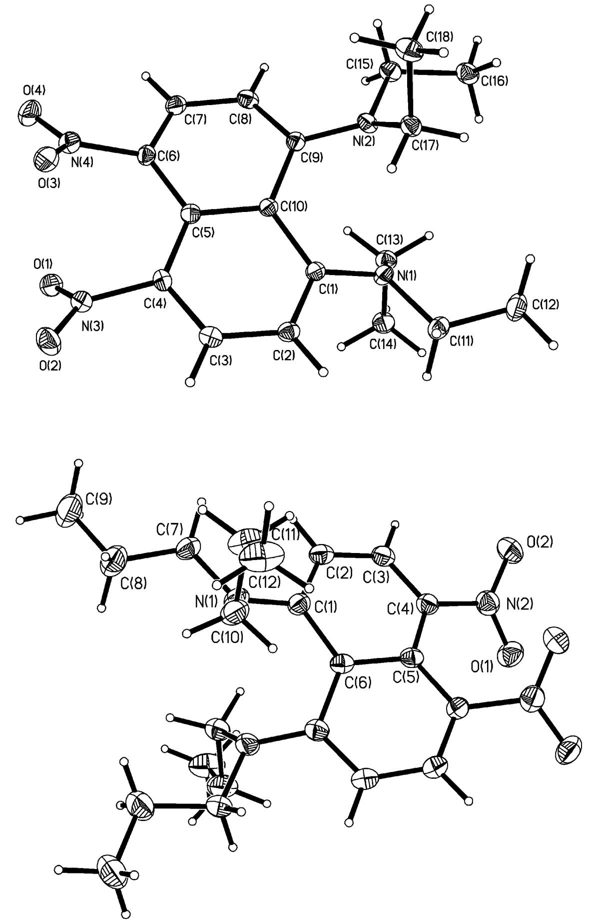
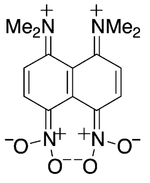


Figure 3. The molecular structures of diethylamino derivative **4** (top) and one of two independent molecules of the dipropylamino compound **5** (bottom) showing thermal displacement ellipsoids (drawn at 30% probability level for non-hydrogen atoms) and the atom numbering scheme.

substituents. To diminish this strain, **2** and **3** adopt conformations in which key structural parameters [the N···N distance, sum of the valent angles at the amine nitrogen atoms (ΣN), the turn angle between the dialkylamino fragment and the naphthalene system (ϕ), the same for the functional groups (CHO or NO_2, θ), and deviation of the amine nitrogens from the mean naphthalene plane (ΔN)] undergo strong changes compared to **1** (Table 1). All this is accompanied by substantial naphthalene ring twisting.

Rather unexpectedly, a number of geometrical parameters evidence that the through-conjugation in the solid *peri*-dialdehyde **2** is more effective than in its *peri*-dinitro counterparts **3**–**5** (Table 1). The most important of them are: 1) the molecule **2** has the largest out-of-plane deviations ($\Delta N > 0.85$ Å) and twisting (helicity) (26°); 2) its NMe_2 groups are more flattened, at the same time being the least turned out relatively to the naphthalene system (cf. ΣN and ϕ values for **2** and **3**–**5**); 3) the N–C_{arom} bonds in **2** are shorter, thus having larger π-component; 4) the N···N distance and the ring distortion in **2** are considerably larger, allowing coplanarity of the functional groups (ϕ = 20°, θ = 16°) and their better π-interaction.

We see three main reasons for these discrepancies. The first one is that the CHO groups are less sterically demanding than NO_2, allowing their greater coplanarity with the ring. The second reason is associated with the stronger Coulomb repulsion of the negatively charged oxygen atoms of the nitro groups in resonance structures of type **3a**. In contrast, in the similar structures for dialdehyde **2**, e.g. **2e**, such repulsion should be weaker due to a larger O^-···O^- distance.



3a

Contrary to our expectations, the effect of temperature turned to be very weak. Actually, at 100 K, both **2** and **3** become a little *more* twisted but no further separation between two donors and two acceptors occurs (see Table 1 for the N···N distances and ΔN values). This may be due to some shortening of the N–C_{arom} bonds in parallel with the in-plane bending of the functional groups because of their less intensive thermal motion. Notably, most of the C–C bonds of molecule **2** at 100 K are longer by 0.003–0.012 Å than at room temperature.

Packing effects may also have substantial influence on the molecular geometry. For example, crystal packing of **3**

Table 1. Main crystallographic parameters of diamines **1**–**5**.

Compound	T [K]	r(N···N)[a] [Å]	r(N–C_{arom})[b] [Å]	ΣN[b] [°]	ϕ[b] [°]	θ[c] [°]	ΔN[b] [Å]	∠ C(2)C(3)–C(6)C(7)[d] [°]
1[e]	room temp.	2.792(6)	1.398(6)	347.1	39.6	–	0.404	11.3
2	296	3.025(2)	1.360(2)	358.2	20.2	16.4	0.859	25.9
	100	3.022(2)	1.359(2)	358.2	19.5	16.4	0.856	26.1
3	250	2.924(2)	1.367(2)	356.3	27.6	30.4	0.665	23.0
	100	2.917(3)	1.367(3)	356.3	28.0	30.4	0.650	23.2
4	120	2.852(3)	1.381(2)	352.5	33.7	40.2	0.554	4.7
5[f]	120	2.829(3)	1.382(3)	350.2	33.6	36.7	0.684	20.6
		2.912(3)	1.392(3)	354.8	30.5	39.4	0.695	20.5

[a] Distance between the amine nitrogen atoms. [b] Average values for two NR_2 groups. [c] Average values for two CHO/NO_2 groups. [d] Twisting of the naphthalene skeleton (∠ ABCD, torsion angle between two C_β–C_β naphthalene bonds named after the conventional "chemical" numbering scheme for naphthalene). [e] Ref.[16]. [f] Data for two independent molecules.

is formed by parallel layers of molecules [all C(5)–C(6) bonds are parallel to the *c* axis] that ensures close head-to-tail dipole-dipole interactions between the dimethylamino and the nitro groups of the neighbouring molecules (Figure 4).[1] These interactions look as if the molecules "pull" or "stretch" each other along the *c* axis and may contribute to their flattening. This effect is not realised in dialdehyde **2**, which has more variable molecular packing. Hence, the molecule of **2** receives more space for in-plane arrangement of its functional groups and out-of-plane twisting of the aromatic system than that in **3**. This is in agreement with the fact that **2** and **3** have very similar cell volumes (near 1380 Å^3) and the cell parameter *c* for **3** becomes *shorter* on heating (see further, Table 5). In addition, the dipole-dipole and π-interactions in **2** are less regular (Figure 4), and its molecular geometry is not dominated by any directed effect.

Surprisingly, the molecular structure of diethylamino derivative **4** is completely different. Although, as expected, its functional groups are substantially less coplanar with the naphthalene π-system ($\phi = 34°$, $\theta = 40°$) than in the dimethylamino analogue **3**, the separation between the amine nitrogens despite the bulkier ethyls is only 2.85 Å (Table 1). However, the most unusual peculiarity of structure **4** is the relative disposition of the NO_2 and NEt_2 groups: in molecule **3** the C–NO_2 bonds appear to be crossing each other; in structure **4** they are directed apart (Figure 5). This difference originates from the shape of the two fused and distorted benzene rings. In the case of **3**, this is an *anti*-"chair-chair" conformation, while structure **4** adopts an *anti*-"boat-boat" form. As such, the overall twisting of the naphthalene moiety in **4** is quite low (<5°).

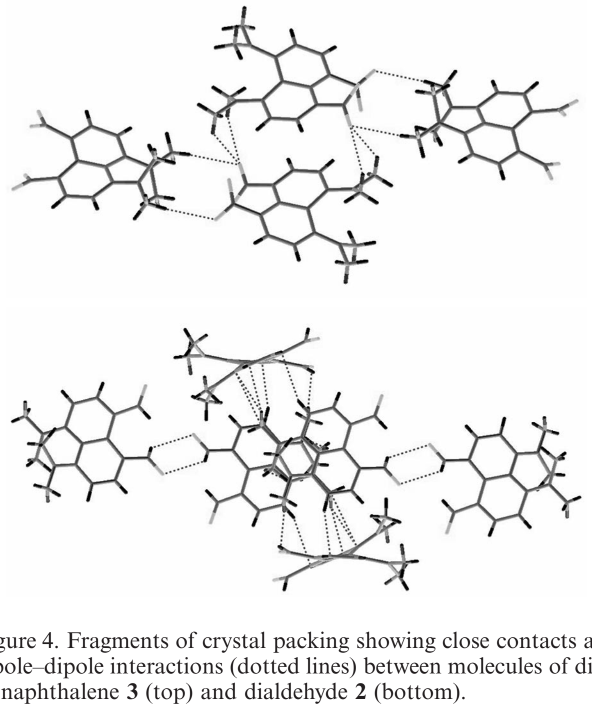


Figure 4. Fragments of crystal packing showing close contacts and dipole–dipole interactions (dotted lines) between molecules of dinitronaphthalene **3** (top) and dialdehyde **2** (bottom).

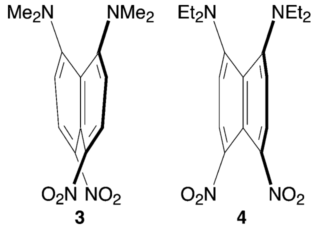


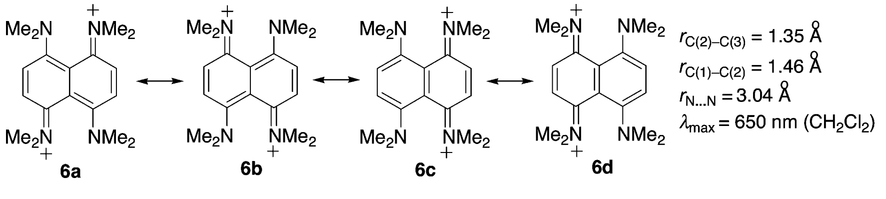
Figure 5. Perspective projections showing crucial differences between molecules **3** and **4**.

Generally speaking, molecule **4** finds alternative way to gain from the through-conjugation, though less effective than in **3**, and to benefit from the crystal packing forces. It seems, in the case of bigger and more flexible substituents, that these forces and crystal surroundings can play a crucial role in governing the resulting conformation of the naphthalene system, as in some *peri*-bis(sulfonamido)naphthalenes.[23] Indeed, in **5**, which has even bulkier dipropylamino groups, the aromatic π-system is again twisted (ca. 21°), and the core molecular structure is close to that of compound **3** but not of **4** (note that the crystals of **4** and **5** were grown up from the same solvent).

To summarise, the resonance π-interaction between the electron donor and acceptor groups in the solid decreases on going from **2** to **5**, yet all structures demonstrate a strong bond alternation within the naphthalene skeleton. Thus, the C(2)–C(3) bonds are all notably shorter than that in the parent proton sponge **1** (see further, Table 4) somewhat reminiscent of quinoid bond systems in such compounds as naphthalene-1,4,5,8-tetrone ($r_{C(2)–C(3)} = 1.32$ Å)[24] or dication **6**, a product of two-electron oxidation of 1,4,5,8-tetrakis(dimethylamino)naphthalene (Scheme 1).[25]

Theoretical Estimations

A convenient way to estimate the extent of conjugation between two functional groups consists in determination of the interaction moment, $\mu^{\pi}_{int.}$, arising from additional charge separation.[26] It represents a difference between the experimental value of dipole moment, μ_{exp}, and the hypothetical value for the same molecule in the absence of any conjugation, $\mu_{add.}$ The latter is calculated by a vector scheme from



Scheme 1. Bond alternation and some properties of dication **6**.

Table 2. Selected calculated structural parameters and dipole moments of proton sponges **2** and **3**.

Compound	μ [D]			$\mu^{\pi}_{\text{int.}}$ [D]			r(N···N)[a]	Angles [°]		
	AM1[b]	PM3[b]	DFT	AM1[b]	PM3[b]	DFT	[Å]	ϕ[a]	θ[a]	ABCD[a]
2	9.88	9.53	9.63	5.82	5.47	5.57	2.885	31.9	14.7	24.2
3	14.48	14.55	12.11	5.28	5.35	2.91	2.862	33.5	29.8	23.7

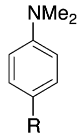
[a] See Table 1 for notations. [b] Calculated with HyperChem v7.1 and with geometries based on cif-generated structures taken at 100 K.

dipole moments of the corresponding functional groups or model compounds including such groups. For example, summation of dipole moments of the proton sponge **1** ($\mu_{\text{exp.}}$ = 1.19 D) and two molecules of 1-naphthocarbaldehyde ($\mu_{\text{exp.}}$ = 2.87 D) gives for the compound **2** $\mu_{\text{add.}}$ = 4.06 D, from which it follows that μ^{π}_{int} = 9.21–4.06 = 5.15 D.

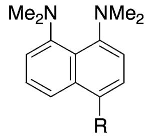
Since experimental measurements of dipole moments for *peri*-dinitro derivatives **3**–**5** were hampered by their low solubility in non-polar solvents, we estimated a μ value for one of them (**3**) by means of quantum-chemical calculations.[27] Preliminarily, it was found that use of methods AM1, PM3 and DFT for *peri*-dialdehyde **2** give satisfactory results, exceeding the experimental value by no more than 3–5% (Table 2). The interaction moments for **2** obtained from these data fall in the range of 5.5–5.8 D. However, in the case of dinitro compound **3**, the theoretical dipole moments are strongly dependent on the calculation method. For example, DFT gives μ = 12.1 D, whereas for AM1 and PM3 it reaches 14.5 D. The additive dipole moment of **3** obtained from the dipole moments of proton sponge and two molecules of 1-nitronaphthalene (4.0 D)[28] is of $\mu_{\text{add.}}$ = 9.2 D. From this, the interaction moments for **3** are 2.9 D and 5.2–5.4 D for the DFT and AM1 (PM3) methods, respectively. In any case, both of these estimates are lower than μ^{π}_{int} for **2**. Thus, for the gas phase, for which theoretical calculations are completed, the tendency of more effective through-conjugation in *peri*-dialdehyde **2** in comparison with *peri*-dinitro compound **3** seems to be valid. Indirectly, this agrees with calculated geometrical parameters of these two compounds, in particularly, with the N···N distances and the ϕ, θ and ABCD angles, although their absolute values in several cases considerably differ from the X-ray data (Table 2).

Solution Behaviour

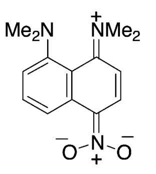
It is well known that through-conjugation between +M and –M-substituents causes an appearance in the UV/Vis spectra of a new long-wave band (K-band), attributed to the π→π* electron transition. Its intensity, ε, mainly depends on the coplanarity of the conjugated groups, and the bathochromic shift (the position of the absorption maxima, λ_{max}) is inversely proportional to the difference between the energies of the highest occupied and the lowest unoccupied molecular orbitals, $E^{\pi\rightarrow\pi*}$. Though, strictly speaking, the latter value refers not only to the ground but also to the excited electron state, it is often used to express the strength of through-conjugation. For example, values of λ_{max} for 4-formyl-**7** and 4-nitro-**8** derivatives of *N*,*N*-dimethylaniline are 342 and 390 nm (in EtOH), respectively.[29] The difference between them ($\Delta\lambda_{\text{max}}$ = 48 nm) testifies that the conjugation in **8** is considerably more effective. A similar situation ($\Delta\lambda_{\text{max}}$ = 56 nm) takes place for monoaldehyde **9** (λ_{max} = 407 nm, MeOH)[14b] and the mononitro derivative of proton sponge, **10** (λ_{max} = 463 nm, MeOH)[30] (Table 3), in which both NMe_2 groups are conjugated.



7 (R = CHO)
8 (R = NO_2)



9 (R = CHO)
10 (R = NO_2)



10a

Unexpectedly, when we switch to the pair *peri*-dialdehyde **2** and *peri*-dinitro derivative **3**, their λ_{max} values in MeOH are practically equal. Notably, although in the dialdehyde the π-interaction sharply increases in comparison with monoaldehyde **9** ($\Delta\lambda_{\text{max}}$ = 42 nm), the two nitro groups in **3** jointly act as a weaker electron acceptor than the sole NO_2 group in **10** ($\Delta\lambda_{\text{max}}$ = –12 nm). At first glance, this phenomenon is not easy to explain because the rotation angles for the NO_2 groups in compounds **3** and **10** are almost the same (θ = 30 and 27°, respectively)[31] and the rotation angles for the NMe_2 groups differ in favour of **3** (ϕ = 28° for **3** against 27 and 36° for 1-NMe_2 and 8-NMe_2 in **10**, respectively).[30] The only reasonable explanation is that the excited state **3a** for compound **3** is strongly destabilised (see discussion above) relative to excited state **10a** for the mononitro analogue. At the same time, as bipolar structure **3a** is obviously more polar than **2e**, it should be more solvated. A conclusive evidence of this point follows from a pronounced positive solvatochromism of nitro compounds **3** and **10** and, in contrast, from its negligible appearance for dialdehyde **2**. As we have already mentioned, the ground

Table 3. Long-wave absorption bands in UV/Vis spectra, λ_{max} [nm] (lgε).

Solvent	**1**	**2**	**3**	**5**	**9**	**10**
MeOH	332 (3.65)	449 (3.52)	451 (–)[a]	454 (4.14)	407 (3.74)	463 (4.02)
$CHCl_3$	341 (3.84)	444 (4.11)	453 (3.87)	–	–	463 (4.10)
DMSO	340 (4.01)	452 (4.16)	476 (3.75)	–	–	484 (4.11)

[a] Exact value of ε could not be measured due to very low solubility.

electron state in the latter is already highly polar, and transition to the excited state is hardly accompanied by such a strong increasing of polarity as in the case of *peri*-dinitro derivative **3**. On the whole, the position of the long-wave absorption maximum for compounds **2** and **3** at best can be interpreted as a result of interplay of several factors, including steric and solvation effects, relative energy of the ground and excited states, as well as the electron acceptor properties of –M-groups (Figure 6). We believe that in solution, due to difference in solvation, the degree of through-conjugation in **2** and **3** is comparable or even somewhat larger for the *peri*-dinitro compound. The spin-spin coupling constants, $J_{2,3}$, in the ^1H NMR spectra of the compounds studied can be considered as independent support of this view. They are known to be proportional to the C(2)–C(3) bond order, and reflect the contribution of the canonical structures of types **2e** and **3a** to the resonance hybrid structure. As one can see from Table 4, the $J_{2,3}$ values for **2** and **3** are equal to 8.4 and 9.1 Hz, respectively (in contrast to the lengths of the same bonds in the solid: 1.37 and 1.38 Å).

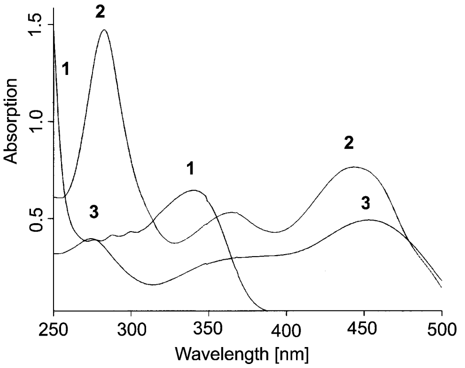


Figure 6. The UV/Vis absorption spectra of proton sponge **1** (c = 9.4×10^{-5} M) and push–pull derivatives **2** (c = 5.9×10^{-5} M) and **3** (c = 6.6×10^{-5} M) in chloroform.

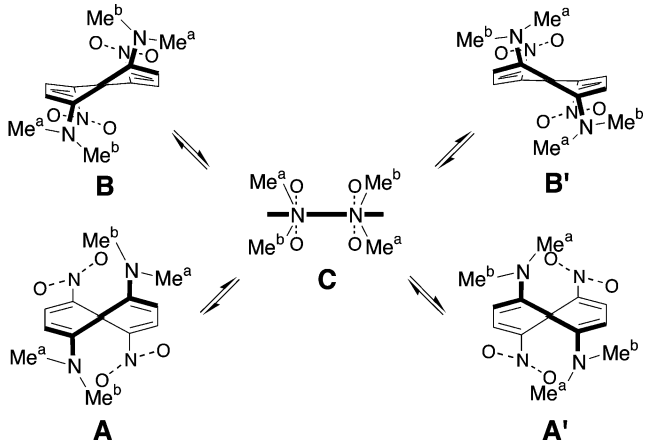
Table 4. Selected ^1H NMR values and X-ray ring C(2)–C(3) bond lengths for proton sponge **1** and its push–pull derivatives.

Compound	δ_H [ppm] (CDCl$_3$) H-2,7[a]	H-3,6[a]	CH$_3$	$J_{2,3}$ [Hz]	$r_{C(2)–C(3)}$ [Å]
1	6.94	7.31	2.81	7.3	1.40
2	6.80	7.93	2.93	8.4	1.37
3	6.73	8.13	2.95	9.1	1.38
	6.85[b]	8.11[b]	2.95[b]	9.2[b]	
4	6.83	8.11	3.33[c]	9.0	1.38
5	6.78	8.12	3.22[c]	8.9	1.37

[a] Hydrogen atoms named after the conventional "chemical" numbering scheme for naphthalene. [b] In [D$_6$]DMSO. [c] N–CH$_2$ group.

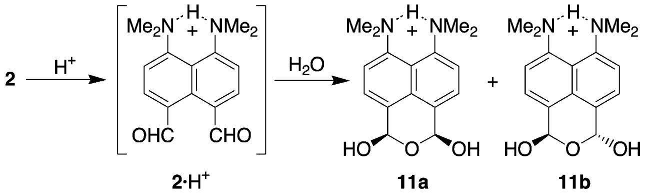
All other ^1H NMR parameters for compounds **2** and **3** are less conclusive. Thus, the δ_H values of the *N*-alkyl groups and especially those of the ring protons are not sensitive to the structural changes. As for the family of dinitro sponges **3**–**5**, the value of $\delta_{H-2,7}$ = 6.83 ppm for ethyl derivative **4** is somewhat out of line with the other ^1H NMR data and in accord with the X-ray diffraction study, indicating the NEt$_2$ groups are aside, and are worse electron donors in this situation than the NMe$_2$ and NPr$_2$ substituents.

As the *N*-alkyl groups in push–pull naphthalenes **2**–**5** are magnetically equivalent at room temperature, one can suggest a fast flipping of the molecules in the NMR time scale. This flipping between the extreme (non-flat) structures of type **A** (**A′**) and **B** (**B′**) through the planar transition form **C** should average all possible conformations in solution (Scheme 2 with compound **3** taken as an example).[32] In the solid state, a highly polar crystal field together with packing forces stabilises conformation **A** (**A′**) for naphthalenes **2**, **3**, and **5** and conformation **B** (**B′**) for compound **4**. In solution, similar stabilisation may occur in the presence of a very polar solvent, as the intramolecular charge separation takes place most completely in conformations of type **A** (**A′**), it is somewhat less effective in conformations **B** (**B′**), while in **C**, with orthogonal substituents, there is no possibility for π-conjugation at all. In fact, the ^1H NMR spectrum of **3** taken in [D$_6$]-DMSO, unlike its spectrum in CDCl$_3$, displays widening of the *N*-methyl peak at δ_H = 2.95 ppm of up to 24 Hz at 20 °C, manifesting the dynamic process. This peak narrows on heating, and is only 2.6 Hz wide at 80 °C.



Scheme 2. Proposed mechanism of interconversion among different conformers of push–pull proton sponges (view along the average ring plane with the amino groups directed toward the viewer).

Since protonation of the basic centres disrupts π-conjugation, this normally affects reactivity of the protonated push–pull systems.[33] Thus, due to effective through-conjugation, dialdehyde **2** seems to be the only stable *peri*-dialdehyde to allow its detailed investigation. However, upon protonation, dialdehyde **2** forms the chelated cation with the NH signal located at δ_H = 18.20 ppm, but no peaks associated with the formyl groups can be found. Instead, a singlet from two OH groups near 3.6 ppm and two singlets near 6.05 ppm assigned for O–C–H protons of *cis*- and *trans*-1,3-dihydroxynaphthopyranes **11a** and **11b** with a 2:3 ratio appear (Scheme 3). Protonation of the push–pull system **2** with an aqueous acid is followed by fast addition of water to cyclise the intermediate cation **2**·H$^+$ into a mixture of protonated naphthopyranes **11**, isolated by us in the form of perchlorates (cf. ref.[14b,34]). This should also eliminate any steric strain and molecular distortions characteristic for **2**, as two pairs of *peri*-substituents in **11** are now involved in formation of six-membered rings.



Scheme 3. Cyclisation of dialdehyde **2** induced by protonation.

Conclusions

We have demonstrated that despite a very large difference in Hammett σ_p constants for NO_2 (0.78) and CHO (0.22) functionalities, two formyl groups in the solid 4,5-bis(dimethylamino)naphthalene-1,8-dicarbaldehyde behave as stronger π-electron acceptors than the two nitro groups in 1,8-bis(dialkylamino)-4,5-dinitronaphthalenes. This phenomenon is attributed to specific *peri*-interactions of the pairs of CHO and NO_2 groups. The former are less sterically demanding, and their through-conjugation with the NMe_2 groups does not result in such strong electrostatic repulsion in the extreme bipolar form as in the case of *peri*-nitro groups. In accordance with theoretical estimations, a similar situation should occur in the gas phase, whereas in solution the π-interaction between the NMe_2 and NO_2 groups is slightly more effective than that between NMe_2 and CHO, evidently due to solvation factors. Several interesting structural anomalies in this proton sponge series have been registered for the first time. All observations made demonstrate that further studies of push–pull proton sponges are rather encouraging.

Experimental Section

Spectroscopic Measurements: UV/Vis spectra were recorded at room temperature with a Varian Cary 100 Scan spectrophotometer. Solution ^{1}H NMR experiments were performed with a Varian Unity-300 spectrometer (300 MHz) with $SiMe_4$ as an internal reference.

Preparation of Starting Materials: The dialdehyde **2** and dinitronaphthalenes **3**–**5** used in this work were prepared according to published procedures: **2**,[14a] **3**,[19,20] **4**.[21] Dipropylamino derivative **5** was obtained as dark orange needles in 19% yield starting from 1,8-bis(dipropylamino)naphthalene[35] following the procedure described for preparation of its ethyl analogue **4**;[21] **5**: m.p. 156–157 °C (EtOH). $C_{22}H_{32}N_4O_4$ (416.52): calcd. C 63.44, H 7.74, N 13.45; found C 63.72, H 7.28, N 13.42.

Reaction of 4,5-Bis(dimethylamino)naphthalene-1,8-dicarbaldehyde with an Aqueous Acid: A 70% aqueous solution of $HClO_4$ (3.2 µL, 0.037 mmol) was added to a solution of dialdehyde **2** (10 mg, 0.037 mmol) in ethyl acetate (2 mL) via micropipette. The resulting heterogeneous mixture was diluted with Et_2O (3 mL). The resulting precipitate was filtered off, washed with Et_2O, dried in air and then under vacuum. This gave a mixture of perchlorates of naphthopyranes **11a** and **11b** (13 mg, 90%) as pale beige crystals with m.p. 179–181 °C (decomp.). ^{1}H NMR ([D$_6$]DMSO): δ = 3.11 (d, $^3J_{NH,NMe}$ = 2.31 Hz, 12 H, NMe_2), 3.64 (s, 2 H, OH), 6.00 (s, 0.6 H, H-1,3 *trans*), 6.09 (s, 0.4 H, H-1,3 *cis*), 7.73 (m, 2 H, H-4,9), 8.13 (m, 2 H, H-5,8), 18.20 (br. s, 1 H, NH) ppm. $C_{16}H_{21}ClN_2O_7$ (388.80): calcd. C 49.43, H 5.44, Cl 9.12, N 7.21; found C 49.56, H 5.87, Cl 9.22, N 7.20.

Theoretical Calculations: DFT calculations were carried out by the restricted Hartree–Fock method with the Gaussian 98 program suite[36] at the B3LYP/6-31G** level of theory.

X-ray Diffraction Analysis: Crystals suitable for X-ray studies were grown by slow evaporation from solutions of compounds in appropriate solvents: **2** (toluene), **3** ($CHCl_3$), **4** and **5** (EtOH). X-ray measurements were conducted with Bruker APEX II (for **2** and **3**) and Bruker SMART 1000 (for **4** and **5**) diffractometers (Mo-K_α line,

Table 5. Crystal data and structure refinement for compounds **2**–**5**.

Parameter	2		3		4	5
Empirical formula	$C_{16}H_{18}N_2O_2$		$C_{14}H_{16}N_4O_4$		$C_{18}H_{24}N_4O_4$	$C_{22}H_{32}N_4O_4$
Formula weight	270.32		304.31		360.41	416.52
T [K]	296(2)	100(2)	250(2)	100(2)	120(2)	120(2)
Crystal system	monoclinic		orthorhombic		monoclinic	orthorhombic
Space group	$P2_1/c$		$Pccn$		$P2_1/n$	$Pnna$
a [Å]	9.2217(5)	9.2013(5)	7.0195(6)	6.9145(10)	7.4837(5)	18.6549(18)
b [Å]	12.3248(7)	12.1591(7)	9.6508(8)	9.6280(14)	14.1303(10)	13.7116(13)
c [Å]	12.7376(8)	12.6146(7)	20.6179(16)	20.620(3)	17.1124(12)	17.4849(17)
α [°]	90	90	90	90	90	90
β [°]	106.5260(10)	106.3440(10)	90	90	96.272(2)	90
γ [°]	90	90	90	90	90	90
V [Å^3]	1387.90(14)	1354.28(13)	1396.7(2)	1372.7(3)	1798.8(2)	4472.4(7)
Z, D_c [Mg m^{-3}]	4, 1.294	4, 1.326	4, 1.447	4, 1.472	4, 1.331	8, 1.237
μ [mm^{-1}]	0.086	0.088	0.109	0.111	0.096	0.086
Reflections collected/unique	13667/2948	12563/2925	13928/1637	12573/1368	17953/4285	48594/6501
R(int)	0.0843	0.0308	0.0483	0.0583	0.0575	0.1358
R_1, wR_2 (all data)	0.0797, 0.1387	0.0487, 0.1031	0.0725, 0.1100	0.1110, 0.1160	0.1049, 0.1298	0.1853, 0.1570
R factor [%]	5.12	3.90	4.69	5.74	5.75	6.92
CCDC number[a]	701234	701233	701236	701235	701237	701232

[a] Data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

graphite monochromator, $\omega/2\theta$-scanning). The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic (for non-hydrogen atoms) approximation. All hydrogen atoms were placed in geometrically calculated positions and were refined in isotropic approximation in the riding model with the $U_{iso}(H)$ parameters equal to $n \cdot U_{eq}(Ci)$ (n = 1.2 for CH and CH_2 groups and n = 1.5 for CH_3 groups), where $U(Ci)$ values are the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded. The main crystallographic data and some experimental details are given in Tables 1 and 5.

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[1] O. Y. Borbulevych, R. D. Clark, A. Romero, L. Tan, M. Y. Antipin, V. N. Nesterov, B. H. Cardelino, C. E. Moore, M. Sanghadasa, T. V. Timofeeva, *J. Mol. Struct.* **2002**, *604*, 73–86.

[2] Y.-J. Zhu, A.-J. Qin, L.-M. Fu, X.-C. Ai, Z.-X. Guo, J.-P. Zhang, C. Ye, *J. Mater. Chem.* **2007**, *17*, 2101–2106.

[3] T. Vijayakumar, I. H. Joe, C. P. R. Nair, V. S. Jayakumar, *Chem. Phys.* **2008**, *343*, 83–99.

[4] T. J. Dines, L. D. MacGregor, C. H. Rochester, *Chem. Phys.* **2006**, *322*, 445–458.

[5] I. Compagnon, R. Antoine, D. Rayane, M. Broyer, P. Dugourd, *J. Phys. Chem. A* **2003**, *107*, 3036–3039.

[6] A. Szemik-Hojniak, I. Deperasinska, W. J. Buma, G. Balkowski, A. F. Pozharsky, N. V. Vistorobskii, *Key Eng. Mater.* **2005**, *277–279*, 1060–1065.

[7] A. Szemik-Hojniak, I. Deperasinska, W. J. Buma, G. Balkowski, A. F. Pozharskii, N. V. Vistorobskii, X. Allonas, *Chem. Phys. Lett.* **2005**, *401*, 189–195.

[8] X. Qian, Y. Xiao, *Tetrahedron Lett.* **2002**, *43*, 2991–2994.

[9] Y. Xiao, X. Qian, *Tetrahedron Lett.* **2003**, *44*, 2087–2091.

[10] L. Jia, Y. Zhang, X. Guo, X. Qian, *Tetrahedron Lett.* **2004**, *45*, 3969–3973.

[11] J. G. Rodriguez, J. L. Tejedor, *J. Org. Chem.* **2002**, *67*, 7631–7640.

[12] S.-M. Wong, B. Shah, P. Shah, I. C. Butt, E. C. Y. Woon, J. A. Wright, A. S. Thompson, C. Upton, M. D. Threadgill, *Tetrahedron Lett.* **2002**, *43*, 2299–2302.

[13] a) A. F. Pozharskii, *Russ. Chem. Rev.* **1998**, *67*, 1–24; b) A. F. Pozharskii, V. A. Ozeryanskii, in: *Proton Sponges*, *The Chemistry of Functional Groups*, *The Chemistry of Anilines* (Ed.: Z. Rappoport), John Wiley & Sons, Chichester, **2007**, part 2, chapter 17, p. 931.

[14] a) N. V. Vistorobskii, A. F. Pozharskii, *Zh. Org. Khim.* **1989**, *25*, 2154–2161; *Chem. Abstr.* **1990**, *112*, 234930m; b) A. F. Pozharskii, G. G. Alexandrov, N. V. Vistorobskii, *Zh. Org. Khim.* **1991**, *27*, 1536–1543; *Chem. Abstr.* **1992**, *116*, 173682r.

[15] R. A. Pascal, *Chem. Rev.* **2006**, *106*, 4809–4819.

[16] H. Einspahr, J.-B. Robert, R. E. Marsh, J. D. Roberts, *Acta Crystallogr., Sect. B* **1973**, *29*, 1611–1617.

[17] Twisting naphthalene to 30° requires 7.2 kcal/mol; see ref.[15].

[18] A. J. Gordon, R. A. Ford, *The Chemist's Companion, the Handbook of Practical Data, Techniques and References*, John Wiley & Sons, New York, **1972**.

[19] T. Barth, C. Krieger, F. A. Neugebauer, H. A. Staab, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1028–1030.

[20] V. A. Ozeryanskii, A. F. Pozharskii, A. M. Fomchenkov, *Russ. Chem. Bull.* **1998**, *47*, 313–317.

[21] L. A. Kurasov, A. F. Pozharskii, V. V. Kuz'menko, N. A. Klyuev, A. I. Chernyshev, S. S. Goryaev, N. L. Chikina, *Zh. Org. Khim.* **1983**, *19*, 590–597; *Chem. Abstr.* **1983**, *99*, 22064v.

[22] Though it was reported[19] that **3** has more than 22° twist in the solid, no other details have been published or deposited with the CCDC.

[23] Z. Olejnik, T. Lis, E. Grech, J. Nowicka-Scheibe, *Pol. J. Chem.* **1998**, *72*, 1255–1268.

[24] F. H. Herbstein, M. Kapon, *Acta Crystallogr., Sect. B* **1982**, *38*, 3123–3125.

[25] T. Barth, C. Krieger, H. A. Staab, F. A. Neugebauer, *J. Chem. Soc., Chem. Commun.* **1993**, 1129–1131.

[26] V. Balasubramanian, *Chem. Rev.* **1966**, *66*, 567–641.

[27] A recent theoretical study [A. J. Gordon, M. H. Palmer, *Mol. Phys.* **2005**, *103*, 2773–2787] on dinitronaphthalene **3** (ab initio MP2 + TZVP) led to rather obscure results which predicted that the naphthalene moiety should be essentially flat with the nitro groups being almost orthogonal to the ring π-system ($\theta >$ 88°). This gives μ = 8.90 D for **3**, which excludes any through-conjugation and is in full contradiction with the experimental data.

[28] J. Y. H. Chau, R. J. W. Le Fevre, *J. Chem. Soc.* **1957**, 2300–2302.

[29] W. D. Kumler, *J. Am. Chem. Soc.* **1946**, *68*, 1184–1192.

[30] A. F. Pozharskii, V. V. Kuz'menko, G. G. Alexandrov, D. V. Dmitrienko, *Zh. Org. Khim.* **1995**, *31*, 570–581; *Chem. Abstr.* **1996**, *124*, 260232c.

[31] For reference: the rotation angles C–NO_2 for 1-nitro- [J. A. Swift, A. M. Pivovar, A. M. Reynolds, M. D. Ward, *J. Am. Chem. Soc.* **1998**, *120*, 5887–5894] and 1,8-dinitronaphthalenes [M. Ciechanowicz-Rutkowska, *J. Solid State Chem.* **1977**, *22*, 185–192] are 23 and 43°, respectively; in contrast, a molecule of naphthalene-1-carbaldehyde is virtually flat [A. F. Pozharskii, *Russ. Chem. Rev.* **2003**, *72*, 447–470].

[32] R. W. Alder, J. E. Anderson, *J. Chem. Soc. Perkin Trans. 2* **1973**, 2086–2088.

[33] V. A. Ozeryanskii, A. F. Pozharskii, W. Schilf, B. Kamieński, W. Sawka-Dobrowolska, L. Sobczyk, E. Grech, *Eur. J. Org. Chem.* **2006**, 782–790.

[34] A. F. Pozharskii, N. G. Tregub, N. V. Vistorobskii, E. Yu. Romanova, Z. A. Starikova, A. I. Yanovsky, *Russ. Chem. Bull.* **1999**, *48*, 1299–1309.

[35] V. A. Ozeryanskii, A. F. Pozharskii, M. G. Koroleva, D. A. Shevchuk, O. N. Kazheva, A. N. Chekhlov, G. V. Shilov, O. A. Dyachenko, *Tetrahedron* **2005**, *61*, 4221–4232.

[36] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98* (Revision A.9), Gaussian, Inc., Pittsburgh PA, **1998**.

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