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peri-Interactions in naphthalenes, 13 [1] 8-Dimethylamino-naphth-1-yl carbinols as model systems for potential N→Si/P interactions

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Abstract

In (8-dimethylamino-naphth-1-yl) ('DAN') carbinols DAN–C(OH)R^1R^2, the N atom can approach the HO group unto N···H-O hydrogen bond distance only when the steric conditions are favourable. The energy gain of such N···H–O interactions is insufficient to force R^1 and R^2 into otherwise unfavourable conformations. The geometry of the naphthalene may cause N, O and C atoms to reside in positions similar to those typical for hydrogen bonds though no N···H–O and N···H–C hydrogen bonds may actually be involved. By analogy, it seems unlikely that in *peri*-donor/acceptor substituted naphthalenes D–$C_{10}H_6$–A dative interactions (D→A) of similar or less energy as such N···H-O interactions can interfere with the geometry conserving forces of naphthalene and the steric effects of the *peri* substituents.

Keywords: peri-Substituted naphthalenes; Intramolecular hydrogen bonds; Weak donor/acceptor interactions; Steric effects

1. Introduction

By definition, the sum of the van der Waals radii of two atoms X and Y, Σr(vdW)[X, Y], is the interatomic distance d(X···Y) at which repulsive forces and attractive van der Waals forces are equal [2,3]. Σr(vdW) presently serves as a measure of the minimum interatomic distance in the absence of other attractive forces. There is a host of different attractive forces which are stronger than the notoriously weak van der Waals forces [3–6] and thus cause d(X···Y) < Σr(vdW) [3,5]. It is, therefore, not possible to conclude from experimentally found d(X···Y) < Σr(vdW)[X, Y] that a *particular* attractive force, such as a dative [two electron] bonding interaction D→A between a σ-electron donor D and an electron acceptor A, is operative [3,6]. There exist even *non*-attractive forces which easily put X and Y (including D and A) into sub-van der Waals distances [2,3]. One of them is the geometry-preserving force of the naphthalene skeleton which tends to be planar and to have bond angles of 120° throughout [2,3, 5–12]. These geometrical features would place equal substituents X in the *peri* positions at a distance of d(X···X) = 246.8 pm and unequal substituents X and Y at a distance of d(X···Y) = ca. 247–255 pm, e.g. d(N···Si) = 251 pm ('*peri distance*', PD) [3,5–11,13]. This is much less than Σr(vdW), e.g. Σr(vdW)[N, Si] = 345 pm [14]. Steric repulsion between X and Y generally forces the naphthalene skeleton into distortion and leads to an increase of d(X···Y) which, however, consistently remains much below Σr(vdW)[X, Y] (e.g. d(N···Si) typically ca. 265–300 pm [15,16]). On the other hand, the naphthalene geometry yields quite easily to strong attractive forces such as the bond length preserving forces exerted by covalent bonds X–Y, e.g. H_2C–CH_2 in acenaphthene, d(C–C) = 154 pm [17], including '*dative*' and even hypercoordinate bonds between D and A, such as N→P, d(N–P) = 213 pm [10]. Hence, both to steric repulsive and covalent bond attractive forces, the naphthalene skeleton is the loser. For a dimethylamino group as a (mediocre [12]) σ-electron donor and a silicon or phosphorus atom as a potential - though doubtful - electron acceptor in 8-dimethylamino-naphth-1-yl ('DAN') silanes and phosphines, the concept of 'a weak dative N→Si/P

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bonding interaction‘ has been promulgated on the basis of $d(\mathrm{N}\cdots\mathrm{Si/P}) < \Sigma r(\mathrm{vdW})$[N, Si/P] though $\gg \Sigma r(\mathrm{cov})$[N, Si/P] ($r(\mathrm{cov})$ = covalence radius) [16,18–20]. A peculiar property of these alleged weak bonding interactions is that unlike conventional covalent bonds they are stretchable ad libitum and can easily assume any bond length between Σr(cov) and Σr(vdW). A linear bond order equation between 1 (Σr(cov)) and 0 (Σr(vdW)) has been devised [21] and applied to DAN-A systems [22]. In our opinion, this very concept seems questionable [2,3,5,10]. At best, only a small bond energy should be associated with a weak bonding interaction [3,6], and the question arises how the naphthalene system would respond to it: would it still yield to the ’bond‘, or would it rather dictate the conditions of such interatomic interaction?

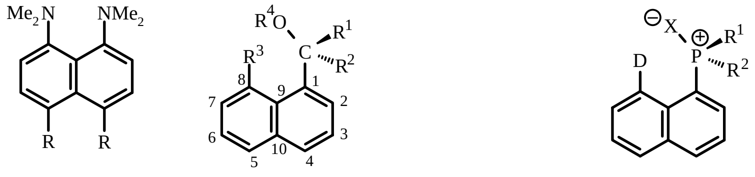
Some insight might be expected from a study of hydrogen bonds. Their bond energies are much smaller than those of covalent bonds. Like the latter, they prefer certain interatomic distances, but they are more amenable to bond length alterations [11], and their bond lengths are within the same range of interatomic distances as those of the alleged N → Si/P bonds. Their potential impact on the naphthalene geometry may therefore be expected to be comparable.

The most prominent DAN compounds to form hydrogen bonds are the protonated proton sponges, first of all 1,8-bis(dimethylamino)naphthalene (**1a**, see Scheme 1) after protonation. For our purpose, however, these compounds are unsuitable, because $d(\mathrm{N}\cdots\mathrm{N})$ of strong $\mathrm{N}\cdots\mathrm{H{-}N}^+$ hydrogen bonds, occasionally as short as 253 pm [23], 256–261 pm in **1a**·H^+[24]), 255 pm in **1b**·H^+[25], is not significantly different from PD [26] and therefore neither able to deform the C_{10} skeleton nor prone to be influenced by the geometry of the latter.

We therefore turned to carbinols DAN-C(OH)R^1R^2 (**2**; see Scheme 1, Fig. 1 and Table 1). In their ideal geometries, the bond lengths and bond angles (120° at sp^2–C, 109.5° at sp^3–C) would permit the O atoms to approach the N atoms unto distances typical for N···H–O hydrogen bonds of moderate strength (or even less). Rotation around the *peri*-C–C bond would give rise to various N···O distances and, in case of N···H–O bond formation, to various bond energies of the hydrogen bonds. These energies might have an impact both on the geometry of the C_{10} skeleton and on the conformations of the *peri*-substituents, mainly concerning rotation of the –C(OH)R^1R^2 group around the *peri*-C–C bond.

In view of Steiner’s *caveat* that not all short O···H–C contacts are hydrogen bonds [27], attention must focus on the possibility that the molecular geometry imposes to the N, O and H atoms interatomic distances and N···H–O angles which are compatible with N···H–O hydrogen bonds but which, unlike the situation in the protonated proton sponges, are not associated with their typical bond energies and hence do not qualify for hydrogen *bonds* in the proper sense. This could be the case when the N-lone pair is not directed towards the H-O bond or, in non-linear N···H–O alignments, does not lie in the N···H–O triangular plane. In DAN–OH, the fact that it does is indicated by its structure with a nearly planar C_{10} skeleton, N, O and H residing nearly in the C_{10} plane and the N-methyl groups nearly symmetrically above and below it in anticlinal (*ac*) positions [28] with respect to the C(1)···C(8) connecting line [29]. Deviations of the Me_2N group from this symmetrical conformation would be indicative of non-coplanarity of the lone pair with the C_{10} plane.

When this project started there was only one crystal structure of a *peri*-carbinol deposited in CSD [7]. In the meantime one of the structures we use in our study, **2a/b** (see Scheme 1 and Fig. 2), has already been published [30]. However, as it was not discussed in the context of steric interactions, we decided to incorporate our results for this compound into this work.



1	R
1a	H
1b	OMe
1c	NMe_2

2, 3	R^1	R^2	R^3	R^4
2a	H	Ph	Me_2N	H (R)
2b	Ph	H	Me_2N	H (S)
2c	DAN	H	Me_2N	H
2d	c-C_3H_5	c-C_3H_5	Me_2N	H
2e	$CHMe_2$	$CHMe_2$	Me_2N	H
3	CMe_3	CMe_3	H	Me

4	D	X	R^1	R^2
4a	Me_2N	O	any	any
4b	Me_2N	S	DAN	Ph
4c	Ph_2P	Se	Ph	Ph

Scheme 1. Definition of compounds.