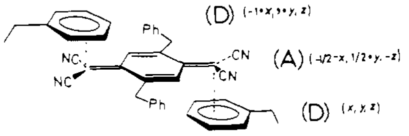
for the strategy underlined in a–e.

Two views that exhibit the striking and unique space architecture of **2** are presented in Figure 1. While the vast majority of weak charge-transfer complexes exhibit infinite stacking motif of the mixed stack type (i.e., ···DADA···),[7] **2** has an entirely different packing motif with regards to the D···A interactions. There are *isolated* "triplets" of the D···A···D type in which the TCNQ moiety of one molecule (in the center of the back face of the cell in Figure 1a) is flanked by two phenyl moieties of two other molecules in the [110] direction as shown in **3** schematically,

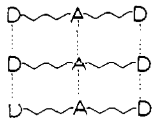


3

with interplanar spacing of 3.44 Å. In addition, the phenyl groups on the central TCNQ in **3** partake in similar D···A···D "triplets" with TCNQ moieties of the molecules at corners of the cell related by [1$\bar{1}$0] forming altogether a two-dimensional network of isolated D···A···D "triplets". Thus each molecule **2** experiences four close-neighbor intermolecular D···A interactions.

Taking an excursion along the *c* direction in space, we find the most striking and unique feature in the space architecture of **2** (Figure 1b). Thus, the central A moieties of the D···A···D triplets *interact among themselves to form an infinite ···AA··· stack along the c direction.* The interplanar A···A distance along the stack is uniform and quite short, at ~3.4 Å, while the overlap is of the $(CN)_2C\cdots C(CN)_2$ type rather than the usual ring–ring or ring–double bond types often found in the segregated stack TCNQ complexes.[7]

This ···AA··· stacking suggests that indeed the intramolecular connectivity of the archetypal molecule **2** exerts enough driving force to push the molecule toward the segregated mode of stacking. In fact, Figure 1b gives the compelling feeling that *the molecular units are really converging to the perfectly segregated stacking motif* (**4**) with *greater overlap between A*'s but are barred by the



4

orthogonality of the TCNQ and phenyl moieties within the molecular unit.

This uniqueness of the structure is likely to find expression in the charge-transfer properties of the solid. Thus, the A···A interactions (LUMO(A)–LUMO(A)) will join the D···A interactions (HOMO(D)–LUMO(A))[1] to enhance the mixing of charge-transfer configurations into the no-bond configuration and thereby increase the degree of electron transfer (ρ). Indeed, the ρ value of **2** obtained from the IR method of Chappel et al.[8a] is ~0.31 while the bond lengths method of Kistenmacher et al.[9] yields $\rho = 0.21 \pm 0.05$[10] While these values should be considered with care,[8b] they clearly are much higher than those for weak charge-transfer complexes[8a] and comparable to those of very strong D–A pairs like TMTSF–TCNQ (red form).[9] In our view this intermediate degree of charge transfer is just a manifestation of the unique architecture of DBTCNQ (**2**).

The structural and electronic features of the archetype **2** all show the promise that upon further proper manipulation of the D moieties (e.g., forming a rigid DAD molecule) the structure will converge to the idealized packing indicated in **4** and thereby will meet requirements a–e, opening a road to a strategic design of molecular conductors with premeditated properties.

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Registry No. 2, 85421-78-9.

Supplementary Material Available: Values for the atomic coordinates, thermal parameters, and bond lengths and angles for DBTCNQ (8 pages). Ordering information is given on any current masthead page.

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[4] A crystal measuring approximately 0.3 mm in diameter was selected for study. Cell constants based on least-squares refinement of 15 reflections (Mo K_α = 0.7107 Å) are a = 13.999 (6) Å, b = 10.760 (2) Å, c = 6.970(2) Å, β = 102.51 (3)°; D_m = 1.23, D_c = 1.25 for Z = 2, M_r 384.5; space group $P2_1/a$. Averaging of 5293 measured intensities yielded 1564 unique reflections with $F > 3\sigma(F)$. The structure was solved by direct methods and refined with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for non-H atoms to R = 0.072. No absorption or extinction corrections were included. All calculations were carried out with the SHELX program package.[5,6]

[5] SHELX76, A Crystallographic Computing Package, G. Sheldrick, University of Cambridge, 1976.

[6] The atomic coordinates, temperature factors, bond lengths, and bond angles appear in the supplementary material.

[7] Herbstein, F. H. In "Perspectives in Structural Chemistry"; 1971; Volume 4, Dunitz, J. D.; Ibers, J. A.; Eds.; Wiley: New York, pp 166–395.

[8] (a) Chappel, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poceler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442. (b) For instance, ν_{CN} for the 2,5-dimethyl and -diethyl derivatives of TCNQ is 2230 cm^{-1}, while that for the 2,5-dimethoxy derivative is 2212 cm^{-1}.[8c] (c) Wheland, R. C., Martin, E. L. *J. Org. Chem.* **1975**, *21*, 3101.

[9] Kistenmacher, T. J.; Emge, T. J.; Bloch, A. N.; Cowan, D. O. *Acta Crystallogr., Sect. B* **1982**, *B38*, 1193.

[10] The relevant bond length parameters (Å) for this calculation are as follows (see ref 9): b = 1.441 (5), 1.456 (5); c = 1.391 (5); d = 1.438 (5), 1.499 (7).

Isotope Effects of Benzylic Deuterons on Chemical Shifts of Ortho Carbons. Correlation with π-Bond Orders as an Indication of a Hyperconjugative Contribution

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There are numerous examples in the recent literature[1] of deuterium isotope effects on ^{13}C NMR chemical shifts. These isotope shifts[2] are of great value as spectral assignment aids, and they are most useful in the elucidation of chemical reaction mechanisms and biosynthetic pathways using deuterium labeled precursors.[3] The majority of deuterium isotope effects on ^{13}C shifts reported so far are shielding, although recently a number of deshielding effects have been observed.[4] Most of these deshielding effects are not intrinsic but are due rather to deuterium-induced perturbations of degenerate conformational equilibria.[4]

In unsaturated systems with deuterium at allylic[7] or benzylic positions,[5,8] deshielding isotope effects occur for the β-carbons and

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[1] For the most up-to-date review on isotope effects on nuclear shielding, see: Hansen, P. E. *Prog. Nucl. Magn. Reson. Spectrosc.*, in press. We thank Dr. Hansen for a preprint of this review.

[2] To achieve a consistent sign convention for isotope shifts, we strongly suggest that the definition should be $\Delta = \delta_{RD} - \delta_{RH}$, i.e., a positive value should denote a high-frequency ("low field") shift in the deuterium compound relative to the reference material (protium compound) as is common usage in defining chemical shifts. Cf. ASTM Standard E 386-76, definition 2.9. For support of this convention, see footnote 3 in the following: Kozerski, L.; v. Philipsborn, W. *Helv. Chim. Acta* **1982**, *65*, 2077–2087.

[3] Recent examples: (a) Abell, C.; Staunton, J. *J. Chem. Soc., Chem. Commun.* **1981**, 856–858. (b) Simpson, T. J.; Stenzel, D. J. *Ibid.* **1982**, 1074–1076.

[4] See the pertinent citations in ref 5 and 6.

[5] Ernst, L.; Eltamany, S.; Hopf, H. *J. Am. Chem. Soc.* **1982**, *104*, 299–300.

[6] Aydin, R.; Günther, H. *J. Am. Chem. Soc.* **1981**, *103*, 1301–1303.

[7] Hansen, P. E.; Led, J. J. *Org. Magn. Reson.* **1981**, *15*, 288–293.

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Table I. Deuterium Isotope Effects[a,b] on ^{13}C Chemical Shifts of Ortho Carbons and C_{ipso}–C_{ortho} π-Bond Orders[c] in Compounds **1–5**

compd	C	isotope shift	bond	π-bond order
1	C-4	−16	C-3/C-4	0.432
2	C-3	−13	C-2/C-3	0.496
3	C-3	−6	C-2/C-3	0.530
4	C-2	+1.6[d]	C-1/C-2	0.667
3	C-1	+15	C-1/C-2	0.782
2	C-1	+18	C-1/C-2	0.806
1	C-2	+20	C-2/C-3	0.859
5	C-2	−6	C-1/C-2	0.782
5	C-8a	+28	C-1/C-8a	0.509

[a] Values given in ppb (0.001 ppm); positive sign denotes deshielding in the deuterated compound. [b] Measured at 100.6 MHz of mixtures of the protium and deuterium analogues; digital resolution better than 0.5 ppb; error estimate $\pm$2 ppb. [c] From INDO molecular orbital calculations (QCPE program No. 141) of benzene, naphthalene, anthracene and furan; experimental geometries used as input. [d] From ref 8.

the para carbons, respectively. These effects and related ones in α-deuterated carbonyl compounds[9] and carbocations[10,11] have been ascribed, at least in part, to diminished hyperconjugative electron release by the C–D relative to the C–H bonds.[5,8–12] Isotope shifts of the ortho carbons in (α-deuteroalkyl)benzenes are explained[8] as resulting from a superposition of the normal ("inductive"[10]) and the hyperconjugative effects.

Isotope effects on NMR chemical shifts would be even more useful if a better understanding could be achieved of their sizes as functions of molecular parameters. We therefore investigated the influence of benzylic deuterons on ortho carbon chemical shifts in compounds **1–4**, in which there is a large variation of double-bond character between C_{ipso} and C_{ortho} but a very similar steric environment of the trideuteromethyl groups. If (hyper)conjugation to some degree influences the sizes of the isotope shifts over three bonds, $^3\Delta$, then one would expect them to depend on the π-bond order, P_π, of the C_{ipso}–C_{ortho} bonds in the same way as regular ortho substituent chemical shifts (SCS) vary with P_π.[13] Our results (Table I) show that for compounds **1–4** the $^3\Delta$ values correlate very strongly with the π-bond order. A least-squares treatment (Figure 1) yields a good linear dependence (correlation coefficient 0.993; root mean square error 1.94 ppb) of $^3\Delta$ on $P_\pi(C_{ipso}–C_{ortho})$:

$$^3\Delta\ (\text{ppb}) = 88.4P_\pi - 54.9 \qquad (1)$$

According to eq 1, low double-bond character involves shielding and high double-bond character involves deshielding isotope shifts over three bonds. This finding fully supports the idea[8] of a superposition of "normal" (negative) and hyperconjugative (positive) contributions to this type of isotope shift. For π bond orders near $^2/_3$ (benzene derivatives) the opposing contributions tend to cancel each other.

Figure 1 also demonstrates that the values of the vicinal isotope shifts in 1-(methyl-d_3)naphthalene (**5**) do not fit the above correlation at all. Since in **5** the CD_3 group is in relatively close contact with the C-8–H-8 bond, this suggests that steric interactions cause substantial alterations of the magnitude of isotope shifts. We have shown previously[5] that nonbonded interactions between deuterons and carbon atoms cause appreciable "through space" isotope shifts. Possible complications by steric factors have thus to be taken into account when trying to predict isotope shifts by means of eq 1.

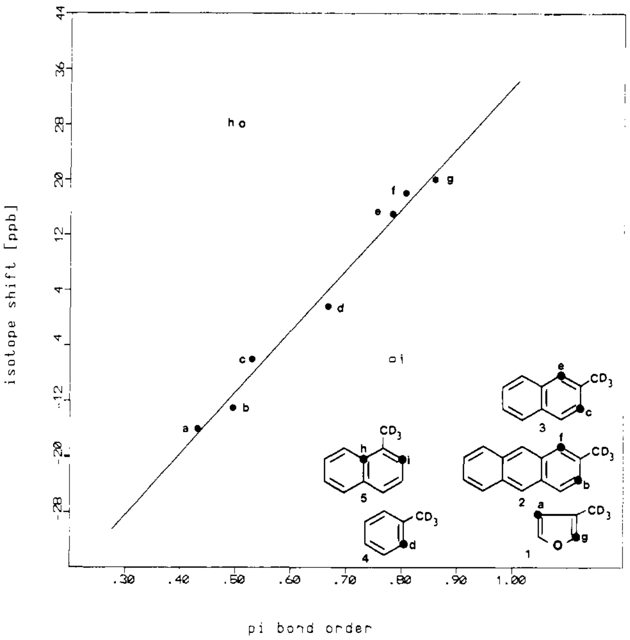

Figure 1. Correlation between the deuterium isotope effects on vicinal carbon chemical shifts and the C_{ipso}–C_{ortho} π bond order in compounds **1–5**. Only points a to g (filled circles) were considered in the calculation of the least-squares line.

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Registry No. **1**, 930-27-8; **2**, 613-12-7; **3**, 91-57-6; **4**, 108-88-3; **5**, 90-12-0.

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(14) Other isotope shifts [ppb]: **1**, −141 (C-3); **2**, −102 (C-2), +13 (C-4a); **3**, −104 (C-2), +12 (C-4a), −5 (C-4), −6 (C-7); **5**, −91 (C-1), −7 (C-4a), −6 (C-5), −7 (C-7), +5 (C-8); one-bond isotope shifts were not determined. Isotope shifts not mentioned were not resolved.

Electron Transfer at Crystallographically Known Long Distances (25 Å) in [Zn^{II},Fe^{III}] Hybrid Hemoglobin

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In this report we describe the first example of long-range electron transfer[1–3] between chromophores that are rigidly held at a fixed *and* crystallographically known distance and orientation. We employ mixed-metal, [M,Fe], hybrid hemoglobins that have both chains of one type, either α or β, substituted with a closed shell zinc(II) protoporphyrin (ZnP), whereas the two chains of the other type contain a ferriheme (Fe^{III}P): [Zn^{II},Fe^{III}].[4] In the

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