reported glycopeptide antibiotics by having a site of carbohydrate attachment on ring F.

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Communications to the Editor

Strategic Design of Organic Conductors. Structure of a Prototypical Molecule

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To design efficient organic conductors composed of donor (D) and acceptor (A) moieties one must achieve the following necessary conditions:[1,2] (a) enforce a segregated mode of stacking ($\cdots DD\cdots| |\cdots AA\cdots$) in the solid state; (b) control the D:A stoichiometry; (c) encode ab initio the desired degree of electron transfer (ρ) into the molecular unit; (d) stabilize the delocalized state, $\cdots D^{\rho+}D^{\rho+}\cdots| |\cdots A^{\rho-}A^{\rho-}\cdots$, below the localized ones (e.g., $\cdots D^{+}D\cdots| |\cdots A^{-}A\cdots$); (e) permit and control the degree of interchain coupling. The systematic control of these conditions will allow the preparation of organic conductors with *predesigned properties*.

The archetypal molecular unit (**1**), which contains both donor

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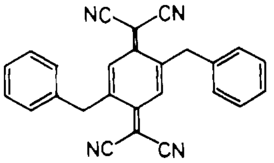
and acceptor moieties in a *prefixed* stoichiometric ratio (n:m), is potentially endowed with the necessary properties that can be manipulated to meet requirements b–d. Thus, for example, a gradual increase of the donor–acceptor abilities of the moieties in **1** will eventually result in an electron transfer whose degree (per D and A) is *predetermined* by the stoichiometric ratio.

The packing of this molecular unit in the solid state may be manipulated by changing the intramolecular connectivity (of D's and A's) in a manner that will eventually increase the propensity of **1** to aggregate in the desired segregated mode of stacking (see a above).

We report here the structure of the primitive member of such a class (D_2A) of molecular units, 2,5-dibenzyl-7,7,8,8-tetracyano-*p*-quinodimethane (DBTCNQ, **2**).[3] As a prototype molecule containing a weak donor (D = phenyl), this material was expected not to be a ground-state conductor ("organic metal") but rather to provide an archetypal D_2A framework for modifications of charge-transfer properties and crystal packing motifs. In both these regards, the crystal structure[4-6] does show promise



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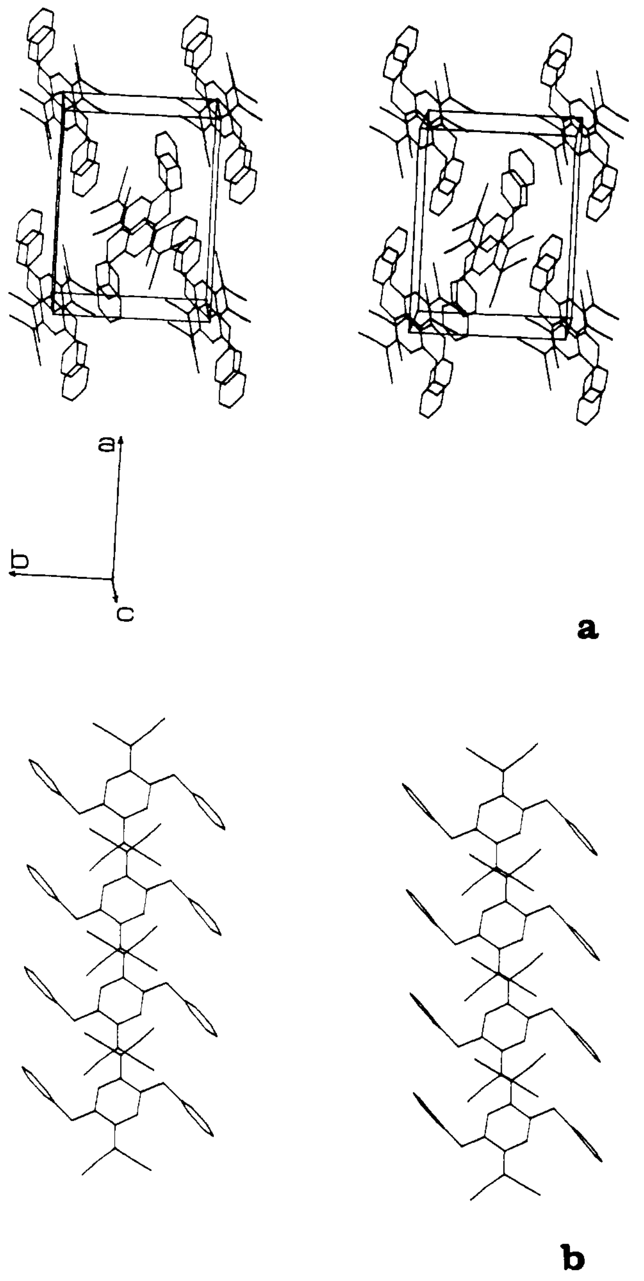

Figure 1. Stereoviews of (a) the unit cell viewed on the *ab* plane (focus on the back face of the cell) and (b) the ···AA··· stacking along the *c* axis which is the line of centers of TCNQ moieties.

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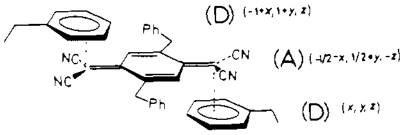
(1) Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 5328.

(2) (a) Perlstein, J. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519. (b) Torrance, J. B. *Acc. Chem. Res.*, **1979**, *12*, 79.

(3) Synthesis will be reported separately in full. It involves dibenzylation of 2,5-bis(ethoxycarbonyl)cyclohexane-1,4-dione with $PhCH_2Br$, hydrolysis, and decarboxylation to yield the 2,5-dibenzyl-*p*-benzoquinone. Treatment of the quinone with $CH_2(CN)_2$ followed by dehydrobromination yields **2** as deep orange crystals (recrystallized from CH_3CN), mp 226–227 °C (Mettler hot stage). Redox potentionals from a voltammogram recorded vs. Ag wire at 100 mV/s in CH_3CN–0.1 M $LiClO_4$ gives two reversible couples: $E_{P_1}{}^{ox} = -0.09$ V, $E_{P_1}{}^{red} = -0.01$ V; $E_{P_2}{}^{ox} = -0.39$ V, $E_{P_2}{}^{red} = -0.32$ V. IR shows ν_{CN} 2213 cm^{-1}.

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,



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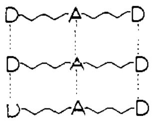
with interplanar spacing of 3.44 Å. In addition, the phenyl groups on the central TCNQ in **3** partake in similar D···A···D "triplets" with TCNQ moieties of the molecules at corners of the cell related by [1$\bar{1}$0] forming altogether a two-dimensional network of isolated D···A···D "triplets". Thus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



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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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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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