J. Org. Chem. 1988, 53, 1689–1694 1689

1,2,3,4-Tetraphenyl[5,6,7,8,9,10,11,12-$^2H_8$]triphenylene (8). The cyclopentadienone 7 (0.104 g, 0.267 mmol) and diphenylacetylene (0.3 g) were heated in a Pyrex screw-capped tube at 300 °C for 2 h. After cooling, the residue was taken up in methylene chloride. Methanol was added, and the product 8 crystallized after partial evaporation of this solution (51 mg, 35% yield). One recrystallization of this material from methylene chloride–acetone gave crystals suitable for X-ray analysis: mp >350 °C (lit.[6] mp [unlabeled] 465°); ^1H NMR ($CDCl_3$) δ 6.68 (m, 4 H), 6.89 (m, 6 H), 7.07 (m, 10 H); MS, m/z (relative intensity) 540 (M^+ [$^2H_8$], 100), 463 ($M - C_6H_5$, 15), 384 ($M - 2C_6H_6$, 10). Isotope ratio analysis indicated that 87% of the molecules contained 8 deuteriums, 10% contained 7, 2% contained 6, and <1% contained 5 or fewer.

X-ray Crystallography. Crystallographic measurements were made on a Nicolet R3m diffractometer at 295 K. Graphite monochromated Cu Kα radiation (λ = 1.54178 Å) was used for crystallographic measurements on 2, and Mo Kα radiation (λ = 0.71069 Å) was used for the measurements on 8. The crystallographic data and details of data collection are reported in Table I. The supplementary material contains more detailed descriptions of the data collection and processing, final atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds 2 and 8.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by an Alfred P. Sloan Research Fellowship (to R.A.P.).

Registry No. 2, 36262-81-4; 6, 113451-49-3; 7, 113474-60-5; 8, 113451-50-6; [$^2H_{10}$]phenanthrene, 1517-22-2; 1,3-diphenylacetone, 102-04-5; diphenylacetylene, 501-65-5.

Supplementary Material Available: Crystallographic data collection and processing descriptions, final atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds 2 and 8 (20 pages). Ordering information is given on any current masthead page.

Synthesis and Properties of Archetypical Donor–Acceptor–Donor (D_2A) Molecules

James Y. Becker, Joel Bernstein, Shmuel Bittner,* Nurit Levi, Sason S. Shaik, and Nirit Zer-Zion

The Organic Metals Group, Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva 84120, Israel

Received June 26, 1987

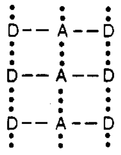
The primary objective of the present investigation was to study a class of compounds in which two donors and one acceptor (D_2A) are parts of the same molecule: **3a–e**. Systematic variation of the donor moiety ($ArCH_2$; Ar = C_6H_5, p-$MeOC_6H_4$, p-$NO_2C_6H_4$, β-naphthyl, p-$NH_2C_6H_4$ (**3a–e**)) leads to a series of compounds that behave in solution to a large extent like substituted TCNQ molecules. In contrast, the isomorphous mode of aggregation in the solid state for **3a**, **3b**, and **3d** indicates a strong driving force toward segregated stacking of the TCNQ moieties, a packing arrangement not observed in other TCNQ derivatives. The solid-state spectral properties also indicate the crucial role of the mode of aggregation. The relevance of these compounds to an overall strategy of design of organic conducting materials is discussed.

Introduction

To obtain conducting electron donor–acceptor (EDA) complexes, several minimal necessary requirements must be met simultaneously.[1-8] Strategies for achieving most of those requirements are known. But ultimately the overall problem is one of multiparameter optimization which is not easily realized, unless by default or serendipity. We have recently proposed[3b] that the molecular unit D_mA_n, 1, in which m donors are linked to n acceptors, possesses sufficient flexibility to optimize simultaneously a few, if not all, of the requirements. The most acute requirement is the architectural problem, namely, the aggregation in the solid state of both donors (D) and acceptors (A) in segregated stacks. Most of the known EDA complexes aggregate in mixed stacks (...DADA...) which are at best semiconductors.[9] Our rationale has been[3b] that for properly designed molecules, of the type 1, the sheer propensity for close packing may exert enough driving force to generate segregated-stack solids. Thus for example a D_2A molecule would have a tendency to produce the solid 2 if this rationale is indeed correct.

D_m---A_n

1



2

In addition, the molecule D_mA_n possesses a potential ρ value which may be fixed by the stoichiometric ratio m/n. Thus, for sufficiently powerful donor and acceptor molecules, n electrons will flow from D_m to A_n to provide an ionic ground state with $\rho_D = n/m$ and $\rho_A = 1$ (if $n < m$).

---

(1) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79.

(2) Perlstein, J. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519.

(3) (a) Shaik, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 5328. (b) Becker, J. Y.; Bernstein, J.; Bittner, S.; Shaik, S. S.; Levy, N. *J. Am. Chem. Soc.* **1983**, *105*, 4468.

(4) Garrito, A. F.; Heeger, A. J. *Acc. Chem. Res.* **1974**, *7*, 232.

(5) Shaik, S. S.; Whangbo, M. H. *Inorg. Chem.* **1986**, *26*, 1201.

(6) Wudl, F. *Acc. Chem. Res.* **1984**, *17*, 227.

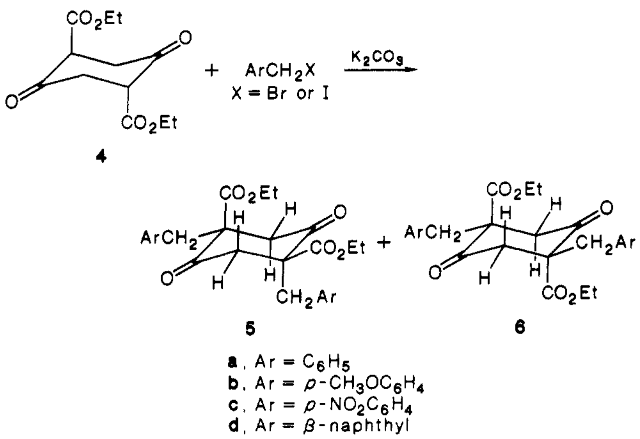
(7) Williams, J. M.; Beno, M. A.; Wang, H. H.; Leung, P. C. W.; Emge, Y. J.; Geiser, U.; Carlson, K. D. *Acc. Chem. Res.* **1985**, *18*, 261.

(8) Whangbo, M. H.; Williams, J. M.; Leung, P. C. W.; Beno, M. A.; Emge, T. J.; Wang, H. H. *Inorg. Chem.* **1985**, *24*, 3502.

(9) (a) Herbstein, F. H.In *Perspectives in Structural Chemistry*; Dunitz, J. D., Ibers, J. A., Eds.; Wiley: New York, 1971; Vol. 4, pp 166–395. (b) Sandman, D. J. *Mol. Cryst. Liq. Cryst.* **1979**, *50*, 235. (c) Even in the family of "organic metals" there are mixed-stack phases: Kistenmacher, T. J.; Emge, T. J.; Bloch, A. N.; Cowan, D. O. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 1193. Emge, T. J.; Bryden, W. A.; Cowan, D. A.; Kistenmacher, T. J. *Mol. Cryst. Liq. Cryst.* **1982**, *90*, 173. Bloch, A. N.; Cowan, D. O.; Bechgaard, K.; Pyle, R. E.; Banks, R. H. *Phys. Rev. Lett.* **1975**, *34*, 1561. Kistenmacher, T. J.; Emge, T. J.; Wiygul, F. M.; Bryden, W. A.; Chappell, J. S.; Stokes, J. P.; Chiang, L.-Y.; Cowan, D. O.; Bloch, A. N. *Solid State Commun.* **1981**, *39*, 415. Emge, T. J.; Wiygul, F. M.; Chappell, J. S.; Bloch, A. N.; Ferraris, J. P.; Cowan, D. O.; Kistenmacher, T. J. *Mol. Cryst. Liq. Cryst.* **1982**, *87*, 137. Aharon-Shalom, E.; Becker, J. Y.; Bernstein, J.; Bittner, S.; Shaik, S. S. *Synth. Met.* **1985**, *11*, 213. Mayerle, J. J.; Torrance, J. B.; Crowley, J. I. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2988.

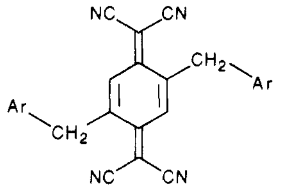
0022-3263/88/1953-1689$01.50/0 © 1988 American Chemical Society

Scheme I



The donor and acceptor abilities can be tuned by substituents on D and A.

Since the architectural requirement is the most acute, we have decided to focus our initial efforts on studies aimed at manipulating the mode of aggregation. The D_2A motif was chosen with A and D being tetracyanoquinodimethane (TCNQ) and aryl moieties connected by CH_2 spacers, as shown in **3** (**3** may also be viewed as a substituted TCNQ). This simple prototype system was designed to test whether the close-packing requirement will exert sufficient driving force to lead to aggregation in the segregated-stack mode, **2**. If this turns out to be the case, then **3** does not behave simply as a TCNQ derivative, for which segregated one-dimensional stacks have not been observed (unless as TCNQ salts[9a]).



3, Ar = C_6H_5, p-$CH_3OC_6H_4$, p-$NO_2C_6H_4$, p-$NH_2C_6H_4$, β-naphthyl

From a different point of view, by suitable variation of the aryl substituents, the ionization potential of the donor (I_D) can be reduced to the point where it is sufficiently low to allow complete electron transfer from D to A. In such a case the solid, **2**, will possess an ionic ground state $(D_2)^+A^-$ ($\rho_D = 1/2$; $\rho_A = 1$). The interplay of the architectural and electronic effects thus holds the potential of producing an isoarchitectural family of D_2A solids, with ground states covering the full range from neutral to ionic.

This paper describes the syntheses and the electrochemical and structural properties of a number of members of the family of compounds belonging to the archetype **3**. These derivatives contain four different aryl groups with increasing donor property. Thus, while none of the donors are powerful enough to generate an ionic ground state, the substituent electronic effect should nevertheless be expressed through the modulation of the energy gap between the neutral ground state and the ionic ground state. Schemes I and II provide the synthetic outlines of these derivatives.

Results and Discussion

Synthesis of Diaryl TCNQ. Ester condensation of 2 equiv of ethyl succinate yielded 2,5-bis(ethoxycarbonyl)cyclohexane-1,4-dione (**4**). This diketo diester was alkylated in acetone in the presence of K_2CO_3 to yield a mixture of the cis and trans 2,5-diaryl derivatives **5** and **6** (Scheme I).[10] These geometrical isomers were separated and isolated in pure form by using either chromatographic methods or fractional crystallization. Assignment of the correct configuration rests upon detailed interpretation of the proton NMR spectra. Examination of the shielding and deshielding effects exerted on the ring methylene groups reveals a distinct difference between the cis and the trans isomers. While in both an AB quartet is expected, the two doublets of the cis isomer are separated by a greater chemical shift difference than in the trans isomer (see Table I). This chemical shift difference can be used for stereochemical assignment. It is also of interest that each cis isomer has a lower melting point than its trans counterpart.

Scheme II

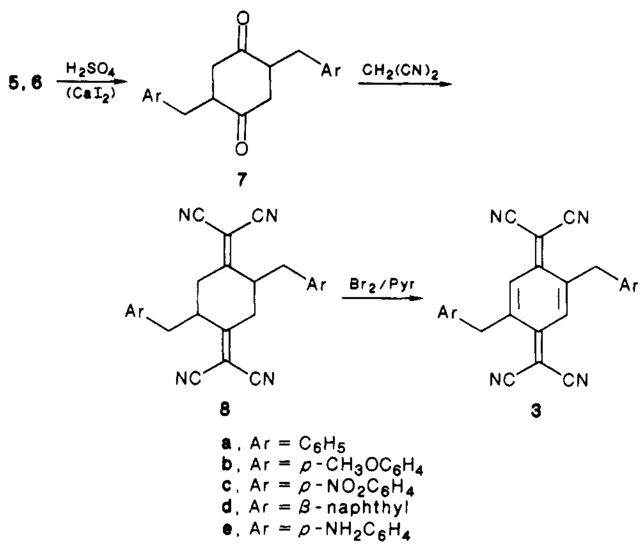


Table I. ^1H NMR Assignment of the Cis and Trans Diaryl Cyclohexanediones 5 and 6

compd	low-field "doublet",[a] δ	high-field "doublet",[a] δ	$\Delta\delta$	geometrical confign
5a	2.90	2.25	0.65	cis[b]
6a	2.88	2.68	0.20	trans[b]
5b	2.85	2.24	0.61	cis
6b	2.84	2.68	0.16	trans
5c	3.04	2.33	0.71	cis
6c	2.89	2.66	0.24	trans
5d	2.98	2.17	0.81	cis
6d	2.95	2.75	0.20	trans

[a] Part of the AB quartet of the ring methylene groups. [b] Reference 10.

Hydrolysis of **5** or **6** of Scheme I was performed in 4 M H_2SO_4 with the minimum amount of ethanol required for dissolution of the compounds.[11] As shown in Scheme II, the hydrolysis was followed by spontaneous decarboxylation to **7** in high yields. Only one isomer of **7** was obtained, probably the thermodynamically more stable trans diequatorial conformer. In some cases (e.g., **5c** and **6c**), the solubility in ethanol was so low that hydrolysis was sluggish and most of the starting ester recovered even after prolonged heating. In such cases, the dione **7** was obtained by cleavage of the β-keto esters with CaI_2[12,13] followed by

---

(10) Chang, D. Y.; Mou, C. C. *J. Org. Chem.* **1974**, *39*, 976.

(11) Anderson, J. R.; Jorgensen, O. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3095.

(12) Chang, D. Y.; Yam, C. F.; Chan, C. Y.; Lee, S. H. *J. Org. Chem.* **1966**, *31*, 3267.

acidification. While the latter is a fast reaction (~1 h), yields are lower than in the hydrolytic methods, and the product is obtained as a mixture of the two geometrical isomers. The *p*-aminobenzyl derivative **7e** was synthesized by $SnCl_2$ reduction of **7c**.

Introduction of the dicyanomethylene group was performed by the usual method,[14,15] using malononitrile/base in a mixture of THF/water. β-Alanine was used as the catalyst since it is basic enough to activate the malononitrile without enolizing the cyclic ketone. The dicyanomethylene products **8** are usually very insoluble compounds which precipitate in good yield from the reaction mixture. They form green-blue complexes with iodine, and their infrared spectra display an intense cyano absorption in the range 2232–2242 cm^{-1}.

The final stage in Scheme II is the formation of diaryl TCNQ **3**, which can be performed either via an addition–elimination pathway with Br_2/Pyr or through direct oxidation, e.g., with dichlorodicyanoquinone (DDQ). bromination–dehydrobromination was effected by using 1.5–2.0 equiv of Br_2 and pyridine in dry acetonitrile at 0–25 °C for 12–20 h to give **3** in moderate to good yields. The same products were also obtained by direct oxidation with DDQ. The two processes appear to be general, and the only failure we encountered was with the *p*-aminobenzyl derivative **8e**. Side reactions prevailed (in either procedure) in this case, and while **3e** was isolated and characterized spectroscopically, it could not be purified satisfactorily for crystallographic solution. It is conceivable that the difficulty in obtaining pure samples of **3e** could be due to reactions of the nucleophilic NH_2 group with the dicyanomethylene group of the TCNQ moiety. Such reactions of nucleophiles with both TCNQ and ethenetetracarbonitrile (TCNE) are well documented.[16]

The color of the $(ArCH_2)_2TCNQ$ solids changes with the donor ability of the aryl group. Thus, for Ar = $p\text{-}NO_2C_6H_4$ the color is transparent yellow. As the donor ability increases, the color changes to transparent orange-red for Ar = C_6H_5, and then to dark violet opaque (with metallic luster) for Ar = $CH_3OC_6H_4$, $NH_2C_6H_4$, and β-naphthyl. The color variation is unique to the solid state and is absent in solutions of **3a–e**. Our preliminary solid-state spectroscopic results show[17] that the color derives from the unique architecture of the solid and originates in a transition from a filled valence band, of the π-type HOMOs of the Ar moieties, to an empty band of the π-type LUMO of TCNQ.[17] Thus, the transition energy decreases as Ar becomes a better electron donor. This trend demonstrates how modification of the substituent can be used to change, in a systematic manner, the gap between the neutral ground state and the ionic excited state. Sufficiently powerful donors may then inverse the energy order of the states and provide a solid with $[(ArCH_2)_2]^+TCNQ^-$ as a ground state. Unfortunately, our lack of complete information on the Ar = $NH_2C_6H_4$ derivative at this stage prevents us from assessing how close we are getting to achieving this state-order inversion. Among the other compounds studied, the most powerful donor (e.g., $p\text{-}CH_3OC_6H_4$) still exhibits a neutral ground state which is per definition nonconducting.

To verify the nature of the ground state of these solids, we utilized the method of Bloch et al.[18] to determine the degree of charge transfer (ρ) from the Ar moiety to the TCNQ moiety. The method employs IR spectroscopy to correlate the vibrational frequency of the CN groups of TCNQ with its ρ value. The IR frequencies of the $(ArCH_2)_2TCNQ$ solids are very close to each other (see Experimental Section) and not far from the frequencies of TCNQ and 2,5-dimethyl TCNQ. The analysis of the frequencies yields ρ values in the range of ~0.2. The low values indicate that all the compounds studied here are essentially neutral solids. However, the nonzero ρ values found for all three compounds are consistent with interaction between the donor Ar moiety and the acceptor TCNQ moiety. The way this interaction is manifested is a result of the unique architecture of the solids.

Table II. Crystallographic Constant for Compounds 3a, 3b, and 3d[a]

	3a	3b	3d
a[b]	13.999 (6)	16.87 (6)	16.98 (3)
b[b]	10.760 (2)	10.235 (6)	11.62 (2)
c[b]	6.970 (3)	7.172 (4)	7.11 (1)
β[c]	102.51 (3)	107.80 (4)	115.3 (1)

[a] Space group $P2_1/a$, $Z = 2$. [b] Angstroms. [c] Degrees.

Crystallographic Studies. The mode of packing in the crystals of these materials is a crucial aspect of their potential ability to conduct electricity. We have noted above the necessary condition of the formation of segregated stacks in order to enable conductivity, and one of the objects of this program is to learn how to control the packing mode of molecules with properties predesigned for their potential to comprise crystals that will conduct electricity. The first member of this series of $(ArCH_2)_2TCNQ$ compounds **3a** was previously found to crystallize in a manner in which the acceptor moieties form infinite segregated stacks.[3b] The near orthogonality of the donor parts of the molecule to the acceptor part apparently prevents the former from forming stacks as well. One aspect of the design of organic conductors is the nature of the molecule, and the series of compounds presented here was designed to examine the effect of changing donor on the molecular properties as discussed above. The second aspect, no less important, of course, is that of the nature of the packing. Does modification of the donor lead to changes in molecular packing? If so, how? If not, why not?

Despite their rather low solubility in most solvents, single crystals for **3a**, **3b**, and **3d** have been obtained. Somewhat to our satisfaction, all three of these compounds are isomorphous, their cell constants being given in Table II.

It is seen that the *c* axis is nearly constant for the three structures, and it is this axis along which the molecules stack as shown for **3a**, **3b**, and **3d** in Figure 1, in which phenyl is used to represent the donors in all the cases. The *a* and *b* axes expand to accommodate the successively larger (than phenyl) anisyl and β-naphthyl moieties. These trends suggest that the packing induces a driving force for the segregated stacking of the TCNQ moiety. The combination of Ar–TCNQ intramolecular orthogonality and $(TCNQ)_\infty$ intermolecular stacking leads to the architectural spine shown in Figure 1, which maintains the Ar_2TCNQ stoichiometry. Note that the isolated aryl moieties shown in Figure 1 are linked to TCNQ moieties which are stacked in the same manner along [110], which is nearly orthogonal to the $(TCNQ)_\infty$ stack shown above in the figure. It is this

---

[13] Chang, D. Y.; Lee, S. H.; Lee, H. C. *J. Org. Chem.* **1967**, *32*, 3716.

[14] Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.

[15] Diekmann, J.; Hertler, W. R.; Benson, R. E. *J. Org. Chem.* **1963**, *28*, 2719.

[16] Ciganek, E.; Lin, W. J.; Webster, O. W. In *The Chemistry of the Cyano Group*; Rappoport, Z., Ed.; Wiley: New York, 1970; pp 463.

[17] Work in progress, in collaboration with Eckhardt, C. K.

[18] Bloch, A. N.; Poehler, T. O.; Chappell, J. S.; Cowen, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442.

Table III. Cyclic Voltammetry Data for 2,5-Disubstituted TCNQ Derivatives[a]

TCNQ substituents	first redox couple[b]			second redox couple[b]			
	E_1^{red}	E_1^{ox}	$E_{1/2}^1$	E_2^{red}	E_2^{ox}	$E_{1/2}^2$	$E_{1/2}^1 - E_{1/2}^2$
H	0.26	0.34	0.30	−0.32	−0.23	−0.28	0.58
Me	0.18	0.28	0.22	−0.36	−0.36	−0.31	0.53
$C_6H_5CH_2$	0.24	0.32	0.28	−0.29	−0.19	−0.24	0.52
p-$MeOC_6H_4CH_2$	0.22	0.30	0.26	−0.28	−0.15	−0.22	0.48
p-$NO_2C_6H_4CH_2$	0.29	0.37	0.33	−0.21	−0.11	−0.15	0.48
β-$NaphCH_2$	0.26	0.32	0.29	−0.29	−0.20	−0.25	0.54

[a] In DMF/0.1 M n-Bu_4NBF_4, on glassy carbon working electrode. [b] All potentials are quoted in volts vs Ag wire quasi-reference electrode (+0.15 V vs SCE). Sweep rate = 1 mV/s. $E_{1/2}$ is defined as $(E_p^{red} + E_p^{ox})/2$. All quoted potentials are averages of two to three separate runs.

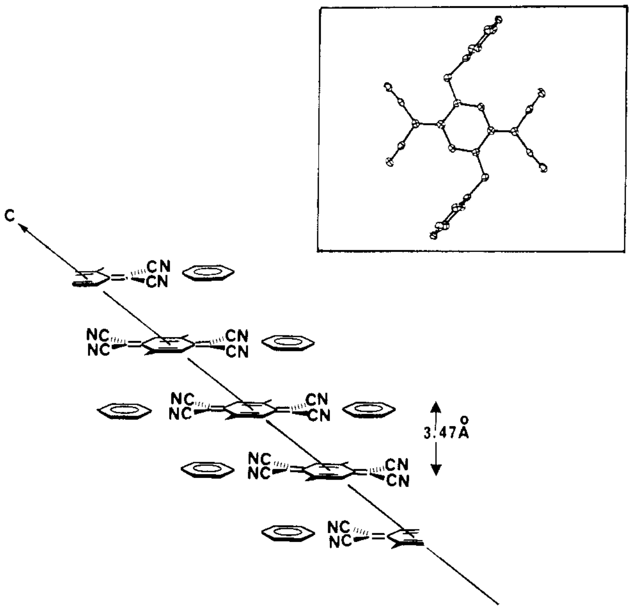


Figure 1. The stacking motif of the **3a**, **3b**, and **3d** $(ArCH_2)_2TCNQ$ derivatives, exemplified for Ar = C_6H_5. Shown are a $(TCNQ)_\infty$ stack along the c axis and two Ar moieties which flank each TCNQ moiety in the stack. The Ar moieties themselves are attached to TCNQ moieties which are also stacked along the c axis but with molecular planes perpendicular to the stack shown here. Shown in a frame is a $(PhCH_2)_2TCNQ$ molecule exhibiting the Ph–TCNQ orthogonality.

intermolecular Ar–TCNQ interaction that gives rise (by HOMO–LUMO orbital interaction) to the significant charge transfer from Ar to TCNQ observed in the crystal spectra. Furthermore, this kind of stacking is not found in the crystal structure of any other TCNQ derivative, unless these are TCNQ salts.[9a] One of our design goals has thus been realized, at least in part.

The full details of the structure solution and discussion of the packing and solid-state spectroscopic properties will be published elsewhere.

Electrochemical Studies. To verify that the Ar substituent exerts only a small perturbation on the TCNQ moiety and that the unique properties derive from the solid-state aggregation, we have carried out electrochemical studies.

The data presented in Table III show that apparently there is only a minor influence of the substituents on the redox properties of the substituted TCNQ derivatives relative to TCNQ. However, the facts that electrochemical data were obtained from one laboratory, by the same person, and by the same cell geometry and the accuracy in measuring the potentials is ±0.01 V suggest that the small differences measured for the redox potentials are significant. If this is the case, then the data for the first redox couple, "$E_{1/2}^1$", suggest that the ease of reduction takes place in the following order of the TCNQ substituent (X): X = p-$NO_2C_6H_4CH_2$ > H > $C_6H_5CH_2$, β-naphthylmethyl > p-$MeOC_6H_4CH_2$ > Me. This order is consistent with that expected from consideration of simple inductive effects, except for the p-$MeOC_6H_4CH_2$ derivative, which was found to be more easily reduced than the Me derivative. The reason for such a deviation from the expected order is not clear.

The above trend of the order in ease of reduction is not fully maintained for the second electrochemical process, "$E_{1/2}^2$". Now, unexpectedly, the derivative with X = p-$MeOC_6H_4CH_2$ is second only to X = p-$NO_2C_6H_4CH_2$. The Me derivative remains the most difficult to reduce in the second electrochemical process as well as in the first.

Conclusions

In several ways the $(ArCH_2)_2TCNQ$ derivatives prepared and characterized here behave in solution as simple TCNQ derivatives. The electrochemical properties show that the TCNQ moiety is as effective an acceptor as unsubstituted TCNQ. This result is in line with the crystallographic observation that on the molecular level the Ar and TCNQ moieties are mutually perpendicular with no substantial interaction. In the same line, the three compounds share, in solution, almost identical electronic spectra of their TCNQ portions. The only unique features of the $(ArCH_2)_2TCNQ$ compounds derive from the solid-state architecture. In this respect, the available evidence strongly suggests that this series of D_2A molecules possess an inherent propensity to generate $(TCNQ)_\infty$ stacks in which the TCNQ moieties are flanked by $(Ar)_2$ moieties, forming triplets of Ar...TCNQ...Ar as shown in Figure 1. The absence of $(TCNQ)_\infty$ stacks in the crystal structures of other substituted TCNQ derivatives indicates that the present stacking motif derives from solid-state packing constraints and not from an inherent electronic propensity of TCNQ to stack. Further work on the amino and other derivatives may ascertain whether we can realize an entire isostructural solid-state family in which the ground state may be changed from essentially neutral to essentially ionic in a systematic way.

Experimental Section

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. The ^1H NMR spectra were recorded on a Bruker WP 200 SY spectrometer in $CDCl_3$ solvent, and chemical shifts are reported in parts per million (δ) downfield from internal Me_4Si. ^{13}C NMR spectra were taken on the same instrument in 12-mm tubes with proton-noise decoupling. IR spectra were taken on a Perkin-Elmer 377 infrared spectrophotometer. For the UV spectra, a Bausch & Lomb, Spectronic 2000 was used. Mass spectra (70 eV) were determined with a Varian MAT 112 instrument. Thin-layer-chromatographic analyses were performed on silica gel 60 F-254 having a 0.2-mm layer thickness. Chromatotron with 2-mm-thick circular plates prepared from Kieselgel 60 PF-254 was used for preparative separations.

All reagents were the best grade commercially available and were used without further purification unless otherwise noted.

Tetrahydrofuran (THF) was dried over Na/benzophenone indicator prior to use. All commercial grade solvents were distilled prior to use.

2,5-Bis(ethoxycarbonyl)-2,5-dibenzylcyclohexane-1,4-dione (5a and 6a). A mixture of 2,5-bis(ethoxycarbonyl)cyclohexane-1,4-dione (64.0 g, 0.25 mol), anhydrous potassium carbonate (49.7 g, 0.36 mol), and benzyl iodide (142.5 g, 0.66 mol) was refluxed in dry acetone (300 mL) for 72 h. TLC (1:1 ether/petroleum ether) showed formation of the two isomers. The mixture was cooled to 0 °C, the salts were filtered off, and the solvent was evaporated in vacuo. The yellowish residue was crystallized from ether/methanol (1:9) to yield 54.0 g (49.5%) of mixture of the two isomers: IR 3000–3100, 2900, 1720, 1610, 750, 700 cm^{-1}. Anal. Calcd for $C_{26}H_{28}O_6$: C, 71.56; H, 6.47. Found: C, 71.45; H, 6.35.

Fractional crystallization from methanol afforded the pure isomers. The cis isomer **5a** crystallized as hexagonal plates melting at 140 °C (lit.[11] mp 140.5 °C): ^{1}H NMR δ 1.25 (t, 6 H, J = 7.0 Hz), 2.25 and 2.90 (q, 2 H, J = 16.0 Hz), 3.12 and 3.27 (q, 4 H, J = 14.0 Hz), 4.15 (m, 4 H), 7.1 (m, 10 H); MS m/z 436 (M$^+$). The trans isomer **6a** crystallized as needles melting at 146 °C (lit.[11] mp 148.5 °C): ^{1}H NMR δ 1.18 (t, 6 H, J = 7.0 Hz), 2.68 and 2.88 (q, 4 H, J = 16 Hz), 3.18 and 3.30 (q, 4 H, J = 14.0 Hz), 4.08 (q, 4 H, J = 7.0 Hz), 7.38 (m, 10 H); MS, m/z 436 (M$^+$).

2,5-Dibenzylcyclohexane-1,4-dione (7a). 2,5-Bis(ethoxycarbonyl)-2,5-dibenzylcyclohexane-1,4-dione (10.0 g, 24 mmol) was suspended in 4 M H_2SO_4 (300 mL) and ethanol (450 mL). Upon heating, a clear solution was obtained, which was refluxed gently for 60 h. Upon cooling, a precipitate formed, which was filtered off. The filtrate was refluxed for another 28 h, cooled, and the precipitate filtered. The combined precipitates (6.3 g, 94%) were recrystallized from THF to give crystals of mp 196 °C: IR 3100, 1690, 720, 700 cm^{-1}; ^{1}H NMR δ 2.56 and 3.21 (q, 2 H, J = 5.5 Hz), 2.6–2.8 (m, 8 H), 7.18 (m, 10 H); MS, m/z 292 (M$^+$). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.19; H, 6.85. Found: C, 82.01; H, 6.68.

1,4-Bis(dicyanomethylene)-2,5-dibenzylcyclohexane (8a). A mixture of 2,5-dibenzylcyclohexane-1,4-dione (2.92 g, 10 mmol), malononitrile (1.94 g, 30 mmol), and β-alanine (0.04 g) was dissolved in THF (20.0 mL) and water (3.0 mL). The solution was refluxed for 12 h and cooled, and water (50 mL) followed by ether (50 mL) was added. White crystals precipitated from the etheric phase and were filtered and washed with ether. The product (2.8 g, 72%) was recrystallized from dimethylformamide and melted at 260 °C. TLC (1:1 $CCl_4/CHCl_3$) gave one spot, which upon exposure to vapors of I_2 gave a green color: IR 3100, 2240, 1600, 750, 720 cm^{-1}; MS, m/z 388 (M$^+$). Anal. Calcd for $C_{26}H_{20}N_4$: C, 80.38; H, 5.19; N, 14.42. Found: C, 80.60; H, 5.38; N, 14.18.

Dibenzyltetracyanoquinodimethane (3a). Bromine (0.9 g, 5.6 mmol) dissolved in acetonitrile (5.0 mL) was added by a syringe, with stirring, to a cooled (0 °C) suspension of 1,4-bis(dicyanomethylene)-2,5-dibenzylcyclohexane (0.97 g, 2.5 mmol) in acetonitrile (10 mL). Pyridine (0.79 g, 10 mmol) dissolved in acetonitrile (2.0 mL) was subsequently added dropwise to the brown solution. The green reaction mixture was stirred at room temperature for 18 h, while the mixture acquired a brown color. Ice-cold water (15.0 mL) was added and stirring continued for an additional 3 h. The precipitate was filtered and washed with cold ether (3 × 5 mL). The product (0.75 g, 79%) was recrystallized twice from acetonitrile to give rhombic orange crystals melting at 226–227 °C: IR 3050, 2213, 730, 690 cm^{-1}; MS, m/z 63, 72, 89, 91, 115, 144, 165, 168, 186, 203, 224, 241, 252, 279, 290, 305, 316, 328, 384 (M$^+$); UV (in CH_3CN) λ_{max} 406 nm (ϵ 54 000 M^{-1} cm^{-1}). Anal. Calcd for $C_{26}H_{16}N_4$: C, 81.25; H, 4.16; N, 14.58. Found: C, 81.16; H, 4.30; N, 14.32.

2,5-Bis(ethoxycarbonyl)-2,5-bis(*p*-methoxybenzyl)cyclohexane-1,4-dione (5b and 6b). *p*-Methoxybenzyl bromide (28.1 g, 0.14 mol) was added to a mixture of 2,5-bis(ethoxycarbonyl)-cyclohexane-1,4-dione (16 g, 62.5 mmol), anhydrous potassium carbonate (12.4 g, 90 mmol), and sodium iodide (1.0 g) in dry acetone (300 mL). The mixture was refluxed gently for 72 h, cooled, and the solvent evaporated in vacuo. To the semicrystalline residue were added methylene chloride (150 mL) and water (150 mL). The two phases were separated, and upon cooling of the organic solution, a precipitate formed, which was filtered and washed with water and with cold methylene chloride. This was proved to be the trans isomer **6b** (3.4 g, mp 188 °C): IR 1720, 1680, 1600, 1110, 1090, 750, 720 cm^{-1}; ^{1}H NMR δ 1.25 (t, 6 H, J = 7.1 Hz), 2.24 and 2.85 (q, 4 H, J = 16.1 Hz), 3.01 and 3.23 (q, 4 H, J = 13.7 Hz), 3.77 (s, 6 H), 4.12 (m, 4 H), 6.73 and 6.88 (q, 8 H, J = 8.8 Hz); ^{13}C NMR δ 13.9, 40.8, 45.0, 55.3, 60.6, 62.3, 114.2, 127.0, 131.3, 159.25, 169.29, 202.24; MS, m/z 496 (M$^+$). Anal. Calcd for $C_{28}H_{32}O_8$: C, 67.74; H, 6.50. Found: C, 67.62; H, 6.72. The total yield was 22.1 g (71.3%).

2,5-Bis(*p*-methoxybenzyl)cyclohexane-1,4-dione (7b). A mixture of 2,5-bis(ethoxycarbonyl)-2,5-bis(*p*-methoxybenzyl)-cyclohexane-1,4-dione (6.0 g, 12 mmol), ethanol (300 mL), and 4 M sulfuric acid (75 mL) was boiled under reflux for 72 h. The mixture was cooled and the precipitate formed filtered off (2.7 g). The filtrate was refluxed for another 48 h, and an additional crop of the product was obtained. The combined yield was 4.0 g (93.0%). Recrystallization from ethyl acetate/methylene chloride (1:9) gave colorless needles, mp 205 °C: IR 3100, 1680, 1600, 1100, 750, 720 cm^{-1}; ^{1}H NMR δ 2.46 and 3.09 (q, 2 H, J = 4.2 Hz), 2.5–2.8 (m, 8 H), 3.78 (s, 6 H), 6.8 and 7.01 (q, 8 H, J = 7.8 Hz). Anal. Calcd for $C_{22}H_{24}O_4$: C, 74.98; H, 6.85. Found: C, 75.05; H, 6.80.

1,4-Bis(dicyanomethylene)-2,5-bis(*p*-methoxybenzyl)-cyclohexane (8b). A mixture of 2,5-bis(*p*-methoxybenzyl)-cyclohexane-1,4-dione (3.52 g, 10 mmol), malononitrile (1.94 g, 30 mmol), and β-alanine (0.04 g) in THF (8 mL) and water (3.0 mL) was boiled under reflux for 16 h. The solution was cooled to 0 °C, and the crude product (4.3 g, 96%) was filtered, dried, and recrystallized twice from acetonitrile and once from ethyl acetate. The pure product (2.5 g, 56%) melted at 262 °C: IR 2238, 1600, 1100, 730 cm^{-1}. Anal. Calcd for $C_{28}H_{24}N_4O_2$: C, 74.98; H, 5.39; N, 12.49. Found: C, 75.29; H, 5.53; N, 12.15.

Bis(*p*-methoxybenzyl)tetracyanoquinodimethane (3b). Method A. Bromine (1.6 g, 10 mmol dissolved in 2.0 mL of acetonitrile) was added to a cooled suspension of 1,4-bis(dicyanomethylene)-2,5-bis(*p*-methoxybenzyl)cyclohexane (0.9 g, 2 mmol) in acetonitrile (10.0 mL). The mixture was stirred at 0 °C while being treated with pyridine (0.8 g, 10 mmol dissolved in 2 mL of acetonitrile). Stirring was continued for 18 h, cold water (20 mL) was added, and stirring was continued for an additional 2 h. The crude product (0.4 g, 46%) was collected and recrystallized twice from acetonitrile. The pure product was obtained as beautiful violet needles with metallic luster melting at 227–28 °C: IR 2212, 1100, 1600, 730 cm^{-1}; UV (CH_3CN) λ_{max} 408 (ϵ 49 999 M^{-1} cm^{-1}), 489 nm (1490 M^{-1} cm^{-1}); MS, m/z 444 (M$^+$). Anal. Calcd for $C_{28}H_{20}N_4O_2$: C, 75.66; H, 4.54; N, 12.61. Found: C, 75.75; H, 4.52; N, 12.48.

Method B. 1,4-Bis(dicyanomethylene)-2,5-bis(*p*-methoxybenzyl)cyclohexane (0.45 g, 1 mmol) was warmed to reflux in tetrahydrofuran (10 mL) under nitrogen atmosphere. Dicyanodichloroquinone (DDQ) (1.0 g, 5 mmol) dissolved in acetonitrile (20 mL) was injected dropwise to the refluxing solution, and heating was continued for 18 h. The solution was concentrated in vacuum to half of its volume and left at 0 °C for 24 h. The precipitating material (0.25 g, 55%) was further recrystallized twice from acetonitrile to give violet needles with mp 228 °C.

2,5-Bis(ethoxycarbonyl)-2,5-bis(*p*-nitrobenzyl)cyclohexane-1,4-dione (5c and 6c). A mixture of 2,5-bis(ethoxycarbonyl)cyclohexane-1,4-dione (32.0 g, 0.125 mol), anhydrous potassium carbonate (24.8 g, 0.18 mol), and *p*-nitrobenzyl bromide (64.8 g, 9.3 mol) in dry acetone (300 mL) was boiled under reflux for 72 h. The precipitating salts were filtered off, and the acetone was evaporated in vacuo to half of its original volume. Cooling of the solution (0 °C, 4 h) caused precipitation of product (23.3 g), which was washed with cold acetone. The solution was evaporated again to half its volume and cooled (48 h), and another crop (12.8 g) was obtained. Total yield was 36.1 g (55%). The cis and the trans isomers were separated by fractional cyrstallization. The cis isomer (**5c**) was obtained in a pure form by recrystallization from methylene chloride (mp 107–108 °C): ^{1}H NMR δ 1.28 (t, 6 H, J = 7.1 Hz), 2.33 and 3.04 (q, 4 H, J = 16.4 Hz), 3.26 and 3.38 (q, 4 H, J = 13.6 Hz), 4.15 (q, 4 H, J = 7.3 Hz); IR 3120, 3080, 1730–1700, 1600, 1515, 1380, 1350, 760, 720, 710, 700 cm^{-1}; MS, m/z 526 (M$^+$). Anal. Calcd for $C_{26}H_{26}N_2O_{10}$: C, 59.32; H, 4.94; N, 5.32. Found: C, 59.36; H, 4.78; N, 5.63. The trans isomer (**6c**) was obtained in a pure form from tetrahydrofuran (mp 227–228 °C): ^{1}H NMR δ 1.15 (t, 6 H, J = 7.1 Hz), 2.65 and 2.90 (q, 4 H, J = 15.1 Hz), 3.34 (s, 4 H), 4.08 (q, 4 H, J = 7.2 Hz), 7.30 and 8.13 (q, 8 H, J = 8.8 Hz); IR 3110, 3090, 1730–1690, 1600, 1510, 1370, 1345, 750, 730 cm^{-1}; MS, *m/z* 526 (M$^+$). Anal. Calcd for $C_{26}H_{26}N_2O_{10}$: C, 59.32; H, 4.94; N, 5.32. Found: C, 59.37; H, 5.19; N, 5.31.

2,5-Bis(*p*-nitrobenzyl)cyclohexane-1,4-dione (7c). 2,5-Bis(ethoxycarbonyl)-2,5-bis(*p*-nitrobenzyl)cyclohexane-1,4-dione (7.8 g, 15 mmol) and calcium iodide tetrahydrate (24.3 g, 72 mmol) were placed in a 250-mL three-necked flask. The flask was flushed with dry nitrogen and heated to 160 °C with stirring. Within a few minutes CO_2 started to evolve and the mixture acquired a brownish color. The foamy mixture was heated for 1 h and the ethyl iodide distilled off. After cooling, dilute hydrochloric acid (100 mL) was added and the product extracted with methylene chloride (2 × 100 mL). The combined organic phases were extracted with water, dried over $MgSO_4$, and evaporated to dryness. The crude yellow solid was recrystallized from tetrahydrofuran to yield 3.3 g (62%) of pure product (mp 246–247 °C): ^{1}H NMR δ 2.5–3.3 (m, 10 H), 7.32 and 8.16 (q, 8 H, *J* = 8.5 Hz); IR 3100, 1720, 1590, 1510, 1370, 1345, 750, 700 cm^{-1}; MS, *m/z* 382 (M$^+$). Anal. Calcd for $C_{20}H_{18}O_6N_2$: C, 62.83; H, 4.71; N, 7.33. Found: C, 62.80; H, 4.84; N, 7.23.

1,4-Bis(dicyanomethylene)-2,5-bis(*p*-nitrobenzyl)cyclohexane (8c). A mixture of 2,5-bis(*p*-nitrobenzyl)cyclohexane-1,4-dione (1.43 g, 3.75 mmol), malononitrile (0.75 g, 11.25 mmol), β-alanine (0.02 g), and water (1.0 mL) in tetrahydrofuran (8.0 mL) was stirred at reflux for 14 h. The precipitating material was filtered and washed with cold tetrahydrofuran and ether. The product (1.4 g, 77%) gave a single spot on TLC and melted at 284–285 °C: IR 3100, 2242, 1600, 1510, 1370, 1345, 750, 730, 700 cm^{-1}; MS, *m/z* 478 (M$^+$). Anal. Calcd for $C_{26}H_{18}N_6O_4$: C, 65.27; H, 3.77; N, 17.57. Found: C, 65.06; H, 3.62; N, 17.52.

Bis(*p*-nitrobenzyl)tetracyanoquinodimethane (3c). 1,4-Bis(dicyanomethylene)-2,5-bis(*p*-nitrobenzyl)cyclohexane (0.48 g, 1 mmol) was warmed to reflux in acetonitrile (10 mL) under a stream of nitrogen. Dicyanodichloroquinone (DDQ) (1.0 g, 5 mmol) dissolved in acetonitrile (15 mL) was injected dropwise to the hot solution, and reflux was continued for 18 h. The solution was cooled to 0 °C, and reduced DDQ (absorbs at 2260 cm^{-1}) was filtered off. From the filtrate precipitated slowly the yellow substituted TCNQ (0.3 g, 62%), which was washed thoroughly with ether and THF and melted at 276 °C dec: IR 3050, 2220, 1590, 1510, 1370, 1345, 790, 750, 720, 700 cm^{-1}; UV (CH_3CN) λ_{max} 405 (ϵ 58800 M^{-1} cm^{-1}), 496 nm (3256 M^{-1} cm^{-1}); MS, *m/z* 474 (M$^+$). Anal. Calcd for $C_{26}H_{14}N_6O_4$: C, 50.63; H, 2.95; N, 5.91. Found: C, 50.72; H, 2.88; N, 5.76.

2,5-Bis(*p*-aminobenzyl)cyclohexane-1,4-dione (7e). A mixture of tin chloride dihydrate (4.0 g, 9 mmol) and concentrated hydrochloric acid (5.0 mL) was warmed to 80 °C, and 2,5-bis(*p*-nitobenzyl)cyclohexane-1,4-dione (0.5 g, 1.3 mmol) was added. The mixture was further heated to reflux for 30 min. The clear solution was cooled to room temperature, and 10% sodium hydroxide solution was added to pH 10. The precipitating product was washed thoroughly with water and then with ether. The product (0.35 g, 83%) melted at 165–166 °C: IR 3420, 3360, 3060, 1700, 1620, 720 cm^{-1}; MS, *m/z* 322 (M$^+$). Anal. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.53; H, 6.83; N, 8.69. Found: C, 74.31; H, 6.80; N, 8.70.

1,4-Bis(dicyanomethylene)-2,5-bis(*p*-aminobenzyl)cyclohexane (8e). In a 20-mL test tube were placed 2,5-bis(*p*-aminobenzyl)cyclohexane-1,4-dione (0.3 g, 0.9 mmol), malnonitrile (0.25 g, 4 mmol), β-alanine (4 mg), and 1 mL of H_2O. The test tube was flushed with dry nitrogen and heated at 110 °C for 15 min. The precipitate that formed upon cooling was filtered and washed with water and then ether to yield 0.2 g (51%) of the product melting at 244–245 °C: IR 3440, 3360, 2236, 1610, 720 cm^{-1}; MS, *m/z* 418 (M$^+$). Anal. Calcd for $C_{26}H_{22}N_6$: C, 74.64; H, 5.26; N, 20.09. Found: C, 74.52; H, 5.18; N, 19.89.

Bis(*p*-aminobenzyl)tetracyanoquinodimethane (3e). Bromine (0.24 g, 1.5 mmol) dissolved in acetonitrile (2.0 mL) followed by pyridine (0.4 g, 5 mmol) dissolved in acetonitrile (2.0 mL) were added to a suspension of 1,4-bis(dicyanomethylene)-2,5-bis(*p*-aminobenzyl)cyclohexane (0.2 g, 0.5 mmol) in acetonitrile (10.0 mL) with cooling and stirring. Upon addition of the pyridine, the solution acquired a dark brown color. Stirring was continued for 21 h at room temperature, then cold water (20 mL) was added, and the mixture was stirred further for 2 h. The precipitate was filtered off and washed with water, acetone, and ether. Attempts to recrystallize the product were unsuccessful. The crude yield was also poor (48 mg, 24%); TLC showed two spots, but chromatographic separation was not successful. The IR spectrum showed the expected absorption: 730, 1600, 2120 (C≡N), 2180 (C≡N), 3360 (NH_2), 3470 (NH_2) cm^{-1}. The MS of the mixture had a strong peak at *m/z* 414, appropriate for the M$^+$ of **3e**.

2,5-Bis(ethoxycarbonyl)-2,5-bis(2-naphthylmethyl)cyclohexane-1,4-dione (5d and 6d). A mixture of 2,5-bis(ethoxycarbonyl)cyclohexane-1,4-dione (25.6 g, 0.1 mol), anhydrous potassium carbonate (17.3 g, 0.125 mol), 2-(bromomethyl)naphthalene (46 g, 0.21 mol), and sodium iodide (1 g) in dry acetone (400 mL) was refluxed gently for 72 h. The salts were filtered off, and upon cooling, the dialkylated compound precipitated from the filtrate (36.4 g, 67%). It was dissolved in dichloromethane (150 mL) and extracted twice with water (100 mL) and twice with 10% NaOH solution. The organic layer was dried over $MgSO_4$, evaporated, and recrystallized from tetrahydrofuran. This was proved (NMR) to be the trans isomer (**6d**) melting at 148–149 °C. The cis isomer (**5d**) was obtained either by recrystallizing the crude product from ethanol or from the filtrate of the trans isomer. It melted at 141–142 °C. ^{1}H NMR (trans isomer): δ 1.02 (t, 6 H, *J* = 7.1 Hz), 2.75 and 2.95 (q, 4 H, *J* = 16.4 Hz), 3.1 (s, 4 H), 3.97 (q, 4 H, *J* = 7.0 Hz), 7.2–7.8 (m, 7 H). MS: *m/z* 536 (M$^+$). ^{1}H NMR (cis isomer): δ 1.27 (t, 6 H, *J* = 7.0 Hz), 2.17 and 2.98 (q, 4 H, *J* = 15.5 Hz), 3.27 and 3.42 (q, 4 H, *J* = 13.0 Hz), 4.15 (dq, 4 H, *J* = 6.5 Hz), 7.05–7.75 (m, 7 H). Anal. Calcd for $C_{34}H_{32}O_6$: C, 71.12; H, 5.97. Found: C, 71.18; H, 5.82.

2,5-Bis(2-naphthylmethyl)cyclohexane-1,4-dione (7d). 2,5-Bis(ethoxycarbonyl)-2,5-bis(2-naphthylmethyl)cyclohexane-1,4-dione (6.2 g, 11.6 mmol) was suspended in 4 M H_2SO_4 (65 mL), and glacial acetic acid (186 mL) was added. The solution was refluxed for 48 h, cooled, and the precipitated crude product (3.2 g, 70%) filtered. It was washed thoroughly with water and then with dichloromethane and melted at 232–234 °C: IR 2840, 1670, 1435, 890, 730 cm^{-1}; MS, *m/z* 392 (M$^+$). Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.71; H, 6.12. Found: C, 85.60; H, 5.96.

1,4-Bis(dicyanomethylene)-2,5-bis(2-naphthylmethyl)cyclohexane (8d). A mixture of 2,5-bis(2-naphthylmethyl)cyclohexane-1,4-dione (0.6 g, 1.5 mmol), malononitrile (0.5 g, 7.7 mmol), and β-alanine (0.03 g) was dissolved in a solvent composed of THF (10 mL), DMF (2 mL), and H_2O (2 mL) and boiled under reflux for 48 h. The solution was cooled to 0 °C, upon which the crude product (0.54 g, 72%) precipitated. The yellow compound was recrystallized from acetonitrile, mp 277–278 °C: IR 2232, 805, 745 cm^{-1}; MS, *m/z* 488 (M$^+$). Anal. Calcd for $C_{34}H_{24}N_4$: C, 83.61; H, 4.92; N, 11.47. Found: C, 83.45; H, 4.66; N, 11.27.

Bis(2-naphthylmethyl)tetracyanoquinodimethane (3d). 1,4-Bis(dicyanomethylene)-2,5-bis(2-naphthylmethyl)cyclohexane (0.6 g, 1.23 mmol) was suspended in acetonitrile, cooled to 0 °C, and bromine (1.3 g, dissolved in 6 mL of acetonitrile) followed by pyridine (1.0 g, dissolved in 6 mL of acetonitrile) were added dropwise. Stirring was continued at room temperature for 48 h, and then cold water (20 mL) was added and stirring of the mixture continued for an additional 2 h. The crude product (0.36 g, 60%) was filtered and washed with acetonitrile. The pure dark violet product melted at 285–286 °C: IR 2220, 1025, 1000, 815, 760 cm^{-1}; UV (CH_3CN) λ_{max} 406 (ϵ 49690 M^{-1} cm^{-1}), 490 nm (2605 M^{-1} cm^{-1}); MS, *m/z* 484 (M$^+$). Anal. Calcd for $C_{34}H_{20}N_4$: C, 84.30; H, 4.13; N, 11.57. Found: C, 84.16; H, 4.27; N, 11.22.

Acknowledgment. This research was supported in part by the Wolf Fund (Israel), the Israel National Academy of Science and Humanities, and the Erna and Victor Hasselblad Foundation (Sweden). We thank one of the revieweres for bringing to our attention ref 16 and for his helpful comments.