Structure Elucidation, Packing, and Solid-State Behavior of the Eglinton – Galbraith Dimer

Uwe H. F. Bunz*[a] **and Volker Enkelmann**[b]

Dedicated to Professor Klaus Müllen

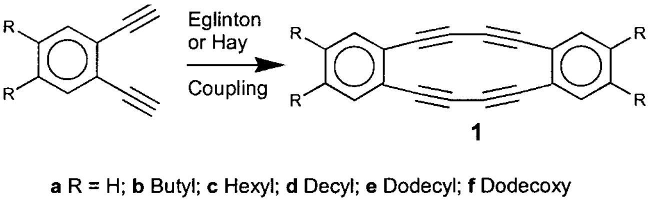
Abstract: Crystal structure, packing behavior, and solid-state activity of the cyclic dimer **1** of *ortho*-diethynylbenzene are described. When crystallized in the presence of TCNQ or hexafluorobenzene, **1** forms novel 1:1 molecular complexes in the solid state. The flat guests are inserted between the disklike molecules of **1** so that mixed stacks are formed.

Keywords: alkynes • crystal engineering • polymerizations • solid-state structures

Introduction

Forty years ago, Galbraith and Eglinton reported that the copper-mediated oxidative coupling of *ortho*-diethynylbenzene furnished the strained yellow macrocycle **1a** (Scheme 1) as the sole isolable product.[1] They noted that crystals of **1a** exploded upon heating or turned black and insoluble when kept under ambient conditions. This reactivity of **1a** was attributed to its highly strained character, expressed by the considerable bending observed in the butadiyne bridges. The identification of **1a** as strained dimer was supported by a low-resolution single-crystal X-ray study by Grant and Speakman.[2] Due to understandable technical problems, the packing behavior of **1a** stayed obscure while its molecular structure could be established.

Surprisingly enough, parent **1a** was never again the target of a structurally oriented study, perhaps due to its purported instability. However, the groups of Swager, Rubin, and Tobe[3] recently reported the synthesis of various substituted derivatives of **1**. Swager undertook a single-crystal X-ray structure analysis of **1b**: the presence of the four butyl groups decidedly stabilizes the cycle; the butyl groups are accommodated best in the packing of **1b**, and dominate the packing pattern. This leads to a molecular packing in which the benzo groups are superimposed and the butyl substituents fill the space above and below the delicate 12-membered octadehydroannulene. This packing arrangement specifically prohibits interactions between the diyne units in different macrocycles by sufficient separation. The substituents thus result in a considerable increase in stability, so that **1b** can be handled under ambient conditions without decomposition. It polymerizes only above 120°C. The crosslinked material obtained showed a strong per signal, but it could not be identified by single-crystal diffractometry. Taking into account the substituents in **1b**, it is clear that intermolecular reactions are attenuated owing to the separation of the butadiyne units by the butyl substituents. It therefore seemed important to examine the packing of **1a** in the light of potential access to crystalline sheet or ladder structures: the synthesis of single-crystalline polymeric materials still represents a major challenge, particularly if two- or three-dimensional covalently linked organic networks are the ultimate targets. These are still unknown, with the exception of Müllen's ladder polymers and Stupps' 2D phases.[4-6]



Scheme 1.

It would be of great interest if **1a,** as a bisdiyne, would display a packing which could lead, by a double topochemical polymerization, to novel sheet and/or ladder polymers.[7a] With these facts in mind, and the hope of solving a classic problem, we undertook the elucidation of the structure and packing of **1a**.

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Results and Discussion

Compound **1a** was synthesized by Swager's method.[3] The yield of **1a** varied between 28 and 37% after chromatography over flash silica gel with a pentane/dichloromethane (9:1) mixture as eluent. The cycle thus obtained was canary yellow and microcrystalline. It could be handled for periods of up to two hours under ambient conditions without apparent decomposition. However, when rubbed vigorously with a metal spatula it exploded.[8] Crystalline needles suitable for single-crystal diffraction could be obtained by slow evaporation of a concentrated solution of **1a** in dichloromethane at 4°C over several days. When the yellow needles of **1a** were stored at 4°C for several weeks under exclusion of light, they turned shiny black and insoluble (chloroform, acetone) under considerable macroscopic bending. According to diffraction experiments, these specimens have lost all single-crystalline order. The reaction product exhibits only broad Debye–Scherrer rings. At room temperature the crystal decomposition occurs within hours after an initial induction period of approximately 12 hours.

In order to prevent thermal decomposition and reaction in the primary X-ray beam, the data collection for **1a** was carried out at 150 K. However, the room-temperature structure could be determined when the data collection time was restricted to 3 hours using a CCD area detector.[9] In Figure 1 the low-temperature molecular structure of **1a** is shown. The butadiyne bridges are bent in accordance with the expected molecular geometry; bond lengths and angles are in excellent agreement with the values described in the literature.[3] The packing of **1a** is shown in Figure 2. The flat molecules are stacked parallel and form columns. These are staggered with respect to each other and form a brick wall motif in the remaining two dimensions, looking straight down the stacks (Figure 2b). Figure 2a depicts the parallel ordering of **1a** in the pillars and shows several independent short intermolecular contacts of the flat molecules in one stack (see dashed lines). The flat, elongated molecular disks pack in a way which would be expected for macroscopic objects of the same shape, indicating that no specific interactions other than van der Waals forces are operative. This packing behavior naturally deviates considerably (vide supra) from that of the bulky **1b** (R = butyl), as the molecules of **1a** pack as in a stack of coins. The analysis of the intermolecular contacts shows that the solid-state reaction is not unique in giving rise to the formation of a disordered crosslinked material.[7c]

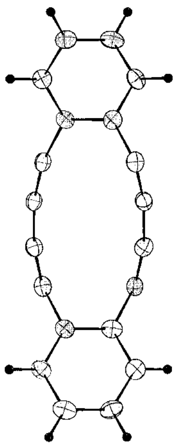


Figure 1. Molecular structure of **1a** at 150 K.

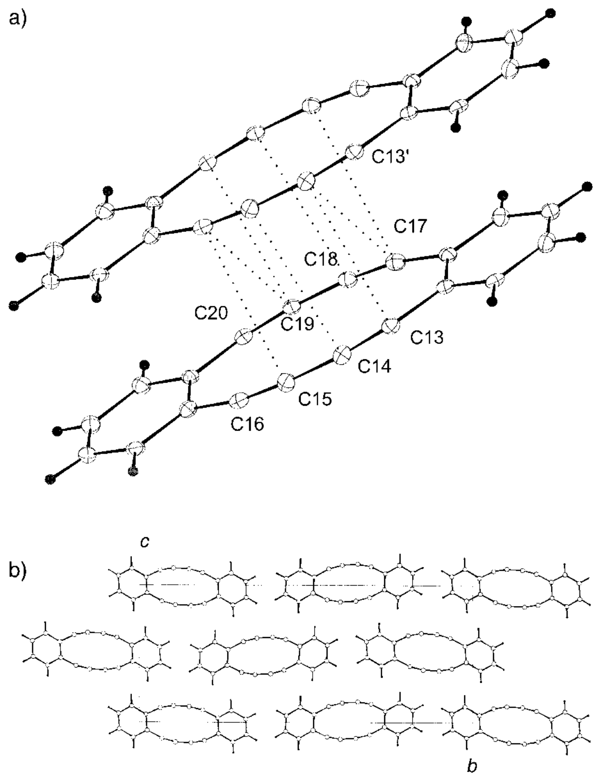
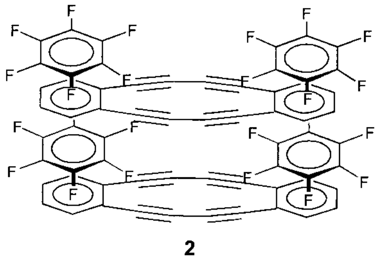


Figure 2. a) Packing of **1a** and close intra-stack distances [Å]: C13–C14' 3.59, C14–C15' 3.69, C15–C16' 3.76, C16–C19' 3.77, C17–C14' 3.80, C17–C18' 3.79, C18–C19' 3.69, C19–C20' 3.58; b) the brick wall motif.

Following this train of thought, we reasoned that it would be interesting to exclude the unwanted intra-stack interactions. This was achieved by separating the molecules by suitable guests. A recent publication by Grubbs and Dougherty[10] describes the successful engineering of interactions between phenyl and perfluorophenyl groups.[11] They seem to interact favorably by ordering parallel to each other due to an advantageous orientation of their quadrupole moments. If this idea is applied to **1a**, cocrystallization with hexafluorobenzene (**3**) should give a layered structure with the composition **1a**·$(C_6F_6)_2$, where the benzo part of **1a** would interact with C_6F_6.



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Abstract in German: *Einkristallstrukturanalyse, Packung und Polymerisationsaktivität des cyclischen Dimers von ortho-Diethinylbenzol werden vorgestellt. Die Kristallisation des Dimers **1a** in Gegenwart von Hexafluorbenzol oder TCNQ führt zu neuartigen 1:1-Komplexen im Kristall, deren Struktur ermittelt werden konnte. Die planaren Gastverbindungen sind dabei zwischen die scheibchenförmigen Moleküle von **1** insertiert, so daß gemischte Stapel entstehen.*

The cocrystallization of **1a** with **3** indeed yields light yellow platelets which are distinctly different from the needles obtained for pure **1a**. Upon isolation from the mother liquor in the atmosphere, these platelets lose **3** with immediate darkening and disintegration. However, if isolated in a sealed capillary under a sufficient partial pressure of **3**, the platelets are stable for extended periods at ambient temperature, even under exposure to X-rays, showing no sign of darkening or loss of crystalline order. The crystal structure of this complex is shown in Figure 3. Surprisingly, the composition is **1a**$\cdot$(C_6F_6). Each of the two types of molecule is located on a symmetry center forming mixed stacks in which **3** is located centrally over the dehydroannulene, and not over the benzo portion of **1a**. No unusual bond lengths and angles are observed. The butadiyne groups are separated by the insertion of **3** so that no intermolecular reaction is possible. Several examples where hexafluorobenzene forms complexes with substituted benzenes have been characterized by X-ray crystallography.[11] In all of the reported cases, the substituted benzenes interact with hexafluorobenzene so that the overlap between the two aromatic nuclei is maximized. A parallel orientation between the two aromatic moieties is always observed. When viewed from top, the molecular images of hexafluorobenzene and the other participating aromatic nucleus, such as mesitylene, appear superimposed. The reason for the unexpected packing behavior of **1** is not entirely clear.[12] In order to shed some light on the packing behavior and its dependence on the electrostatic potentials in **1a**$\cdot$(C_6F_6), we performed a semiempirical calculation (MOPAC, AM1 Hamiltonian) on both compounds to extract the partial charges on the constituent rings (Figure 3b; dark is positively charged, light is negatively charged). In hexafluorobenzene, the ring is positively charged, while the fluorine substituents carry some negative charge, as expected. In the cyclic bisdiyne the situation is more interesting, insofar as the alkyne-carrying carbons are positively charged, while all other carbon atoms in **1a** are negatively charged. As is visible in Figure 3b, the observed packing does satisfy the electrostatic potentials to a certain extent. The naive packing arrangement suggested in **2** would create considerably more electrostatic repulsion because of the required match of the negatively charged fluorine substituents with the likewise negatively charged alkynyl arms of **1a**.

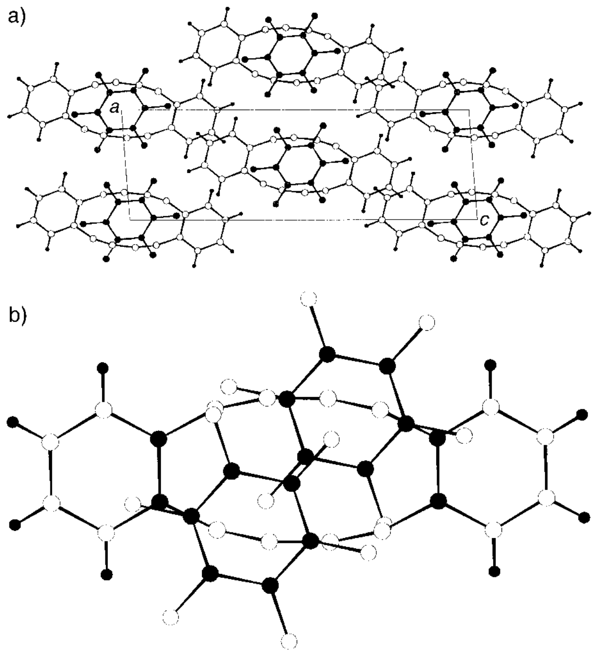

Figure 3. a) Molecular structure of **1a**$\cdot$hexafluorobenzene; b) electrostatic potentials of **1a**$\cdot$hexafluorobenzene; dark: positively charged atoms; light: negatively charged atoms.

After the successful complexation of **1a** by **3** we tried to form CT complexes[13] of the Eglinton dimer with the anhydride of pyromellitic acid (**4**) and tetracyanoquinodimethane (TCNQ). While **4** did not form a molecular complex with **1a** upon cocrystallization, slow evaporation of a solution of **1a** and TCNQ in acetone/dichloromethane at 4 °C gave rise to small, blue-green, single-crystalline needles suitable for X-ray diffraction. When **1a** and TCNQ were mixed together, a light yellow solution formed; the blue-green color is only observed in the solid state. The crystals were surprisingly stable and did not show any sign of solid-state polymerization or crosslinking under ambient conditions. Neither were they sensitive towards loss of the guest, due to the negligible vapor pressure of TCNQ.

As in the case of the C_6F_6 solvate, the structure is a 1:1 complex consisting of mixed stacks of the reaction partners. The insertion of the TCNQ molecules separates the butadiyne groups so that no reaction is possible. The packing diagram is shown in Figure 4; TCNQ is inserted between two molecules of **1a** in a perfectly symmetric way, so that the aromatic nucleus of TCNQ is positioned directly over the dehydroannulene, while the cyano groups are positioned over the benzo rings.[12] To a good approximation the thermal motion of the molecules can be described in all structures by a rigid-body vibration model.[14] The eigenvalues of the **L** tensors are given in Table 1. While the librational amplitudes for **1a** and TCNQ are fairly small and decrease with temperature in the expected manner, C_6F_6 exhibits an appreciably higher motion. The mean-square librational amplitude of 10° at room temperature suggests that hexafluorobenzene performs 60° rotational jumps at this temperature.

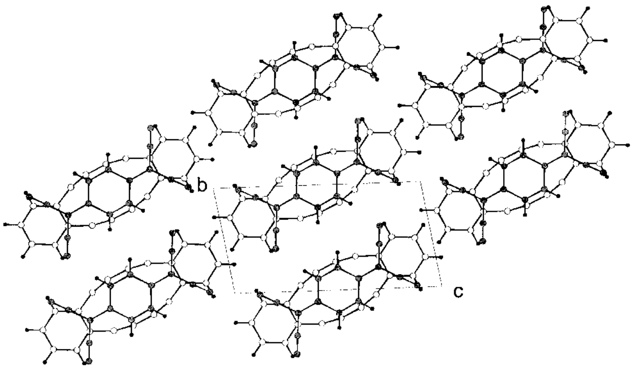

Figure 4. Packing arrangement of **1a**$\cdot$TCNQ.

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Table 1. Eigenvalues of the librational tensor ($^{\circ 2}$).

Structure	T [K]	**L**1 (**1a**)	**L**2 (**1a**)	**L**3 (**1a**)	**L**1 (guest)	**L**2 (guest)	**L**3 (guest)
1a	RT	1.75	4.11	25.21	–	–	–
1a	150	0.56	2.28	12.43	–	–	–
1a·TCNQ	RT[a]	3.79	6.32	30.91	0.77	3.85	42.87
1a·TCNQ	RT[b]	3.44	6.35	30.25	0.53	3.53	41.83
1a·(C_6F_6)	RT	2.55	4.50	20.97	20.71	28.18	104.5
1a·(C_6F_6)	165	1.35	2.40	14.17	10.48	11.99	36.24

[a] Structure determination CAD4 ($Cu_{K\alpha}$ radiation). [b] Structure determination KCCD ($Mo_{K\alpha}$ radiation).

Conclusion

We have been able to solve the structure of the Eglinton–Galbraith dimer **1a**. We showed that its solid-state reactivity is not, as assumed initially, a property of the individual molecule due to the strained nature of the bent butadiyne bridges, but is merely guided by the packing arrangement of the diyne groups.[15] In the course of this study we have learned that **1a** readily forms cocrystals with **3** or TCNQ which are robust under ambient conditions. The guests can be envisioned as molecular insulating sheaths for **1a**. This behavior should be general and not restricted to **3** or TCNQ and should give rise to novel organic layered hybrid materials.[16]

In future we will look for novel packing arrangements in other cyclic and acyclic bisdiynes and examine their ability to form sheet-like solid-state structures and/or solid-state complexes with other guests.

Acknowledgments

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[9] Crystallographic data: **1a** (room temperature): orthorhombic, $P2_12_12_1$, $a = 3.872(1)$, $b = 11.537(1)$, $c = 28.165(2)$ Å, $V = 1258.2$ Å^3, $Z = 4$, $\rho = 1.311$ g cm^{-3}, $\mu = 0.694$ cm^{-1}, 1721 unique reflections, 899 observed, $R = 0.050$, $R_w = 0.045$. Data collection with $Mo_{K\alpha}$ radiation, Nonius KCCD diffractometer. **1a** (150 K): orthorhombic, $P2_12_12_1$, $a = 3.822(1)$, $b = 11.410(1)$, $c = 28.126(2)$ Å, $V = 1226.4$ Å^3, $Z = 4$, $\rho = 1.345$ g cm^{-3}, $\mu = 5.505$ cm^{-1}, 1584 unique reflections, 1093 observed, $R = 0.087$, $R_w = 0.097$. Data collection with $Cu_{K\alpha}$ radiation, Nonius CAD4 diffractometer. **1a·TCNQ** (room temperature): triclinic, $P\bar{1}$, $a = 7.117(1)$, $b = 7.069(1)$, $c = 12.665(1)$ Å, $\alpha = 94.555(5)$, $\beta = 100.783(5)$, $\gamma = 113.265(5)^{\circ}$, $V = 566.7$ Å^3, $Z = 2$, $\rho = 1.326$ g cm^{-3}, $\mu = 0.745$ cm^{-1}, 2234 unique reflections, 1395 observed, $R = 0.039$, $R_w = 0.039$. Data collection with $Mo_{K\alpha}$ radiation, Nonius KCCD diffractometer. **1a·TCNQ** (room temperature, second determination): triclinic, $P\bar{1}$, $a = 7.114(1)$, $b = 7.062(1)$, $c = 12.636(1)$ Å, $\alpha = 94.561(5)$, $\beta = 100.774(5)$, $\gamma = 113.273(5)^{\circ}$, $V = 564.6$ Å^3, $Z = 2$, $\rho = 1.331$ gcm^{-3}, $\mu = 5.959$ cm^{-1}, 2326 unique reflections, 1668 observed, $R = 0.042$, $R_w = 0.051$. Data collection with $Cu_{K\alpha}$ radiation, Nonius CAD4 diffractometer. **1a·C_6F_6** (room temperature): monoclinic, $P2_1/n$, $a = 6.442(1)$, $b = 7.425(1)$, $c = 19.893(2)$ Å, $\beta = 95.010(5)^{\circ}$, $V = 947.9$ Å^3, $Z = 4$, $\rho = 1.522$ g cm^{-3}, $\mu = 1.229$ cm^{-1}, 2351 unique reflections, 1211 observed, $R = 0.057$, $R_w = 0.082$. Data collection with $Mo_{K\alpha}$ radiation, Nonius KCCD diffractometer. **1a·C_6F_6** (165 K): monoclinic, $P2_1/n$, $a = 6.3286(8)$, $b = 7.3391(9)$, $c = 19.786(1)$ Å, $\beta = 94.503(3)^{\circ}$, $V = 916.1$ Å^3, $Z = 4$, $\rho = 1.574$ g cm^{-3}, $\mu = 11.378$ cm^{-1}, 1825 unique reflections, 1361 observed, $R = 0.053$, $R_w = 0.064$. Data collection with $Cu_{K\alpha}$ radiation, Nonius CAD4 diffractometer. The structures were solved by direct methods (Sir 92) and refined by full-matrix least-squares analyses with anisotropic temperature factors for all non-hydrogen atoms. The H atoms were refined in the riding mode with isotropic temperature factors. For those structures determined with $Cu_{K\alpha}$ radiation an empirical absorption correction was applied to the data. Further details of the crystal structure analyses can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-410532 – CSD-410537.

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