

Prediction of new donors for organic superconductors

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Abstract

The donors of all known one- or two-dimensional organic superconductors are based on a core organic molecule that is either tetrathiafulvalene (denoted as TTF) or tetraselenafulvalene (denoted as TSeF) or some mixture of these two molecules. Coupling X , with appropriate acceptors, Y , leads to superconductivity. The oxidized form of X may be X^+ or X_2^+ species in the crystal. From ab initio quantum mechanical calculations (HF/6-31G**), we find that all known organic superconductors involve an X that deforms to a boat structure while X^+ is planar. This leads to a coupling between charge transfer and the boat deformation phonon modes that we believe is responsible for the superconductivity of these materials. Based on this idea we have developed similar organic donors having the same properties and suggest that with appropriate electron acceptors they will also lead to superconductivity.

Keywords: Donors; Superconductors

1. Introduction

Several organic superconductors have been developed using the donors in Fig. 1(b)–(d), coupled with ap-

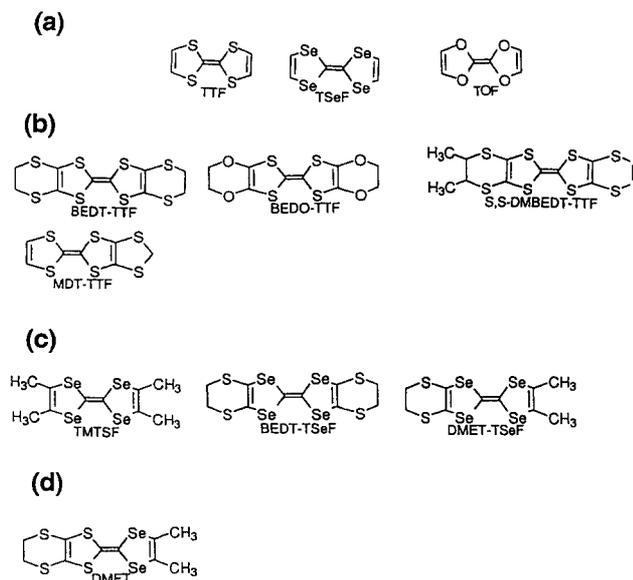


Fig. 1. (a) Tetrathiafulvalene (TTF), tetraselenafulvalene (TSeF) and tetraoxafulvalene (TOF); (b) TTF-based donors of organic superconductors; (c) TSeF-based donors of organic superconductors; (d) TTF–TSeF mixed donors (DMET) of organic superconductors.

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propriate acceptors [1–3]. These are all based on S- or Se-containing fulvalenes (tetrathiafulvalene, TTF, and related molecules in Fig. 1(a)). The superconducting transition temperatures, T_c , range up to 12.8 K and have improved slowly over the years. Despite the advances in T_c , progress in developing new materials is impeded by the lack of an understanding of how the superconductivity is related to fundamental structural quantities. Herein we identify what we believe is the salient structural issue in the superconducting coupling mechanism and use this insight to suggest a number of new donors, all of which are expected to show superconductivity when coupled with appropriate acceptors. These donors are simpler than the current ones and some may lead to higher T_c values.

2. Results and discussion

In most systems the donors form dimers X_2 so that there is one hole per dimer. The holes on the dimers result in overlapping valence and conduction bands, leading to electrical conduction involving both positive and negative charge carriers.

We have used ab initio quantum mechanics [4–6] (Hartree–Fock, 6-31G** basis) to examine the structures for a number of donors in both the oxidized (X^+) and neutral (X) states and find that all known donors for

superconductors lead to a distorted boat conformation (see Fig. 2) for X and a planar conformation for X^+ . As an electron hops from X to X^+ , the original X distorts from boat to planar, while the original X^+ distorts from planar to boat. This leads to a coupling between conduction electrons and vibration (phonons) that is, we believe, the salient coupling for superconductivity. The idea is illustrated in Fig. 3. For two X molecules and one hole, the electron transfer is coupled to a simultaneous boat distortion. In the crystal this leads to processes as in Fig. 4, which considers an excess electron on one dimer in a sea of normal X_2^+ dimers.

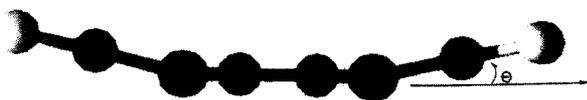


Fig. 2. Side view of the boat structure for Cl-TTF. The optimum angle is $\theta = 14.3^\circ$.

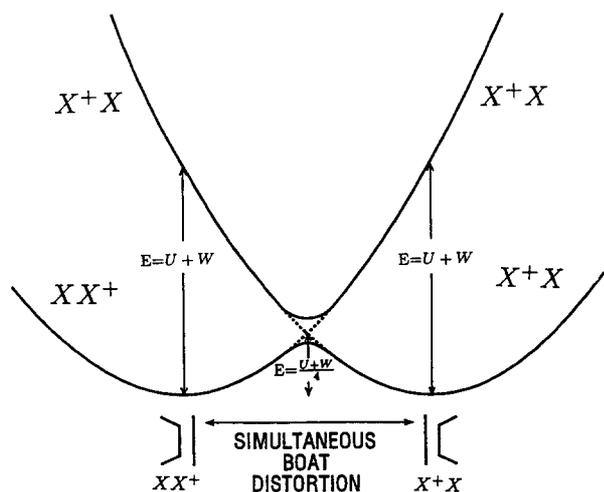


Fig. 3. Marcus-type electron transfer diagram for $XX^+ \rightarrow X^+X$. Electron transfer from XX^+ to X^+X is coupled to simultaneous boat distortions for both molecules, $\omega = \omega_b + \omega_b^+$. This strong coupling between conduction electrons and vibration is the basis for superconductivity.

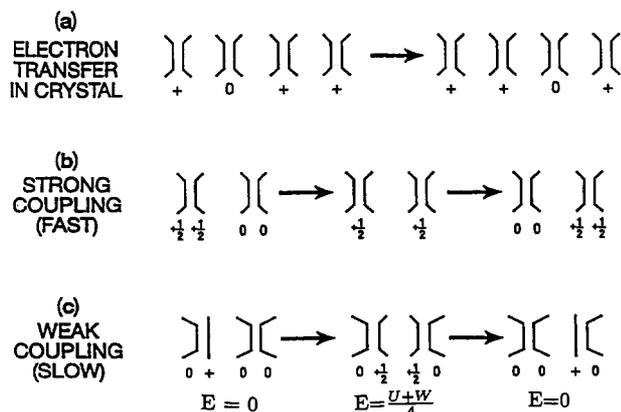


Fig. 4. Illustration of electron transfer in X_2^+ superconductors: (a) the case of one extra electron; (b) the structural changes for fast transfer; (c) the structural changes for slow transfer.

Based on these considerations we hypothesize that TTF-like molecules which lead to boat-distorted neutral donors (but a planar positive ion) will result in superconductivity when combined with suitable acceptors. Here we use this idea to suggest several new donors as candidates for forming superconductors. The simplicity of these new donors might lead to improved properties.

The donors for the known superconductors (Fig. 1(b)–(d), all based on TTF, TSeF, or a mixture) are all expected to have distorted neutral donors. However, we find that the parent compounds of Fig. 1(a) are all planar in the neutral (and oxidized) forms. Thus, none of the donors in Fig. 1(a) would lead to the coupling such as in Figs. 3 and 4, responsible for superconductivity. Only upon replacing the hydrogen atoms of the TTF and TSeF molecules with bulky groups do we get distortions.

The results of calculations for several substitutions are summarized in Table 1. We expect that the superconducting T_c is related to the distortion angle θ , boat stabilization ΔE_{boat} and boat vibrational frequency,

Table 1

The deformation angle, θ (see Fig. 2), energy difference between boat and planar structures, ΔE_{boat} , and the lowest boat deformation vibrational frequency, ν_{boat} , for various organic donors

Species	Substitution ^a	θ^b ($^\circ$)	ΔE_{boat} (meV)	ν_{boat}^c (cm^{-1})
TOF		0.0	POS ^d	76.1
	Cl	0.0	POS ^d	29.7
TTF		0.0	+14.39 ^{d,e}	17.7
	F	11.3	NEG ^f	18.6
	Cl	14.3	-5.87	18.1
	CH ₃	5.8	-0.18	10.3
TSeF	Cl	15.5	-5.74	n.a.
	CH ₃	7.9	-0.40	n.a.
BEDT-TTF		21.1	-28.36	19.5
	Se ₅	24.4	NEG ^f	n.a.
	O ₆	8.5	NEG ^f	10.5
	O ₅	0.0	POS ^d	21.5

^a For TTF or TSeF, all substitutions replace H atoms with the corresponding substituents. For BEDT-TTF, the subscripts show that the S atoms in the five- or six-membered rings are replaced by Se or O.

^b For ET-derived molecules with C_2 symmetry, θ is the average angle on both sides of the central plane.

^c n.a. = frequencies not yet calculated.

^d POS indicates that, starting with C_2 symmetry, the optimized structure becomes a planar structure; hence, the energy of the boat structure is higher than the planar structure.

^e To obtain the positive ΔE_{boat} , we started with the optimized planar and boat structures containing Cl and replaced each Cl with H as the appropriate distance.

^f NEG indicates that, starting with C_2 symmetry, the structure optimizes to a boat structure; hence, the energy of the boat structure is lower than the planar structure. However, we did not separately optimize the planar structure to obtain ΔE_{boat} .

ν_{boat} . Generally, we expect that larger θ , ΔE_{boat} and ν_{boat} will lead to higher T_c (as long as the positive ion is planar and the system is a conductor).

Replacing the H in TTF with Cl or F leads to substitutional distortions (14 and 11°, respectively). Cl–TSeF leads to a distortion larger by 1.2° but Cl–TOF is planar. These results are consistent with the studies on BEDT–TTF (i.e., ET) where S or O in the six-membered ring (the same position as in the Cl in Cl–TTF) leads to distortion. In addition, replacing the S in the five-membered ring with Se leads to larger distortions, but replacing S with O in the five-membered ring leads to no distortion. For TTF and TSeF replacing the H with CH₃ also leads to a small distortion (6 and 8°, respectively), but little energy lowering.

The origin of these distortions is found in the bond angle preferences of the atoms involved. The bond angles in OH₂, SH₂ and SeH₂ are 104.5, 92.1 and 90.6°, respectively [7]. On the other hand, the average angle in the five-membered rings is $540/5 = 108^\circ$. Indeed, for the molecules in Fig. 1(a), the optimum angles are 105.01 and 95.09° at O and S, respectively. Thus, S and Se lead to a significant strain energy. Although planar, these molecules (with S or Se) are spring loaded, needing only additional steric interactions to tip the balance toward nonplanar. Although not calculated, TTeF is expected to yield even larger distortions (probably about 17°) for Cl substitution.

Cl–TTF has a distortion 3° larger than F–TTF; Br–TTF and I–TTF should lead to even larger distortions. This is consistent with the results on BEDT–TTF where replacing S₆ with O₆ leads to much smaller distortions. Thus, for BEDT–TTF, replacing S₆ with Se₆ or Te₆ should lead to increased distortions. Similarly, although CH₃ leads to only a small distortion for TTF and TSeF, we expect that tBu (i.e., C(CH₃)₃) would lead to much larger distortions.

We have ignored packing issues. The ET-based systems crystallize into structures with two-dimensional layers of ET dimers separated by a two-dimensional layer of acceptor molecules. The positive hydrogen atoms of ET interacting with the negative acceptor layer probably play a role in stabilizing this structure. The modified molecules such as Cl–TTF are halogen terminated, leading to a net negative charge in the region of the acceptor. This would likely require hydrogen on the acceptors to attract electrostatically the negative halogens. Thus, I₃ and Cu(NCS)₂ would likely not be good acceptors for Cl–TTF. On the other hand,

with tBu groups the standard acceptors might be satisfactory.

3. Conclusions

(i) We indicate a criterion for determining new classes of donors, namely, that the neutral molecule distorts into a boat form, while the cation species is planar.

(ii) We suggest several new candidate donors for organic superconductors, each involving simple modifications of TTF and related molecules.

Tests of these suggestions should provide additional insights into the mechanism of superconductivity and might lead to improved properties.

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Some of these calculations were carried out on the JPL-Cray computer.

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