On the existence of long C–C bonds between pairs of anions which repel: when and why? A test case on the $[TCNE]_2^{2-}$ dimers found in ionic crystals†

Paper

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Many of the $C_m[TCNE]_n$ (C = cation) salts have intradimer C–C interactions in the range of 2.9 to 3.5 Å and show the electronic fingerprints associated with C–C bond formation (IR and UV spectra, magnetic properties, structural changes), despite the fact that two $[TCNE]^{\bullet-}$ anions should repel each other due to purely Coulombic considerations. Herein, we analyze these pairwise interactions in detail for a particular crystal in which such a C–C bond is found, to understand when and why these bonds are formed in a general case.

1. Introduction

Understanding the exact nature of all the intermolecular interactions present in crystals of technological interest is necessary to rationally design materials with improved technological properties. Strong organic electron acceptors (A), *e.g.*, tetracyanoethylene (TCNE), 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), perfluoro-7,7,8,8-tetracyano-*p*-quinodimethane ($TCNQF_4$), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), *etc.* form stable electron transfer salts that contain $[A]^{\bullet-}$. These strong acceptors A have the common features of being planar and having two reversible one-electron reductions. Among these salts, many are of interest because of their magnetic, conducting and in some cases superconducting properties.

The analysis of the crystal packing of the $C_m[TCNE]_n$ (C = cation, TCNE = tetracyanoethylene) salts sometimes shows the presence of π–π dimers (hereafter identified as π-$[TCNE]_2^{2-}$), like those found in the structure of the $[Et_4N][TCNE]$ electron transfer salt (Fig. 1).[1] The π-$[TCNE]_2^{2-}$ dimers found in this crystal show a nearly coplanar disposition of the monomers (the C(4)–C(1)–C(2)–C(6) dihedral is 169.0°, while the C(3)–C(1)–C(2)–C(5) dihedral is 164.6°), with the shortest C–C distance between the monomers being 2.827 Å. The central C–C bond on each $TCNE^-$ monomer is 1.418 Å, and the CN groups move out of the $TCNE^-$ plane by 6.6°.[1] Thus, C(3), C(4), C(5), C(6) deviate from the nominal plane that contains C(1) and C(2) by 0.266 Å. These dimers are nominally centrosymmetric. Similar dimers have been reported in twelve additional structures,[2] with the average intradimer C–C distance between the two $[TCNE]^-$ fragments being 2.90 Å. As shown in Fig. 1, close to the π-$[TCNE]_2^{2-}$ dimers are two monocharged Et_4N^+ cations (the H atoms are not shown), which preserve the electrical neutrality of the $[Et_4N]_2[TCNE]_2$ crystal.

The central issue in this paper is establishing if the 2.827 Å intradimer C–C distance found between the monomers of the π-$[TCNE]_2^{2-}$ dimers in the $[Et_4N]_2[TCNE]_2$ crystal is a bond. Why are we interested in investigating the bond nature of these C–C contacts, if they lie well outside the commonly accepted range for the usual C–C covalent bonds? The reason is that, despite their long C–C distance, we have found (see below) that they present all the common spectroscopic features generally associated with the presence of a conventional covalent C–C bond. For instance, the dimers are diamagnetic as expected if a bond is formed. Furthermore, there are geometrical changes that occur as expected if a new C–C bond were made between the two fragments of the dimer. Thus, we investigate where the spectroscopic features come from, and the nature of the interactions in the π-$[TCNE]_2^{2-}$ dimers, to establish whether we have to extend the distance range of the conventional covalent C–C bonds, have a new type of C–C bond, or have a no-bond situation which shares some of the physical features of a bond. We are going to explore in detail these facts for $[Et_4N]_2[TCNE]_2$.[1]

2. Experimental evidence on the nature of the $[TCNE]_2^{2-}$ dimer in the $[Et_4N]_2[TCNE]_2$ crystal

$[Et_4N]_2[TCNE]_2$, Fig. 1, is a prototype of a π-$[TCNE]_2^{2-}$ dimer that can be used to illustrate and rationalize their physical

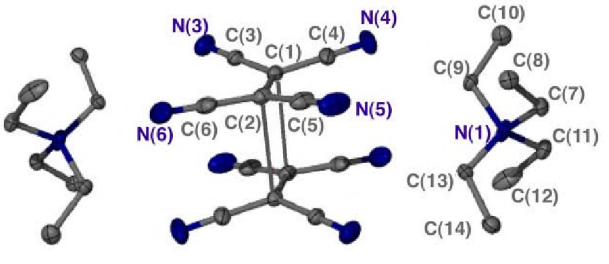

Fig. 1 Atom labeling and thermal ellipsoid (40%) plot of $[Et_4N]_2[TCNE]_2$ showing its π-$[TCNE]_2^{2-}$ dimer. H atoms and disordered alkyl chains omitted for clarity. Key bond distances and angles are C(1)–C(2) 1.418(3) Å, C(1)–C(2)′ 2.827(3) Å, C(1)–C(3) 1.424(3) Å, C(1)–C(4) 1.418(3) Å, C(2)–C(5) 1.425(3) Å, C(2)–C(6) 1.432(3) Å, C(3)–N(3) 1.149(3) Å, C(4)–N(4) 1.145(3) Å, C(5)–N(5) 1.146(3) Å, C(6)–N(6) 1.150(3) Å; C(1)–C(2)–C(1)′ 90.2(2)°, C(2)–C(1)–C(2)′ 89.8(2)°, C(3)–C(1)–C(4) 118.5(2)°, C(5)–C(2)–C(6) 117.3(2)°, C(1)–C(2)–C(5) 120.7(2)°, C(1)–C(2)–C(6) 120.7(2)°, C(2)–C(1)–C(3) 120.3(2)°, C(2)–C(1)–C(4) 119.9(2)°; C(4)–C(1)–C(2)–C(6) 169.0(2)°, C(3)–C(1)–C(2)–C(5) 164.6(2)°.[1]

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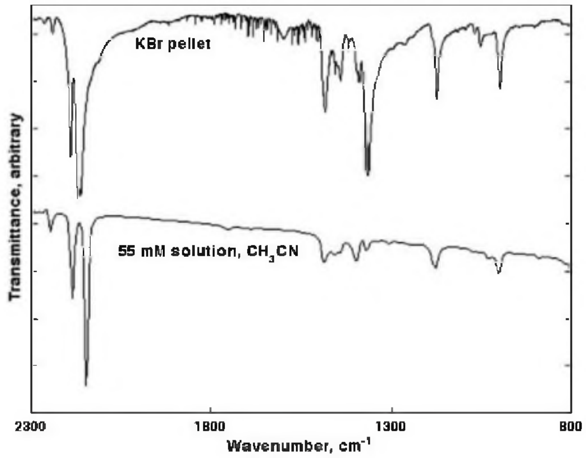

Fig. 2 Solid state IR spectra of $[TCNE]_2^{2-}$ in a KBr pellet of $[Et_4N]_2[TCNE]_2$, and in a low concentration solution of CH_3CN, where $[TCNE]^-$ dimerization does not occur.

properties and the causes of their existence. The IR spectrum of π-$[TCNE]_2^{2-}$ in $[Et_4N]_2[TCNE]_2$ (Fig. 2) differs with respect to its fragments, *i.e.*, π-$[TCNE]_2^{2-}$ exhibits three νC≡N vibrations at 2191 (m), 2170 (s), and 2163 (s) cm^{-1} and νCC at 1365 (s) cm^{-1}. The 1365 cm^{-1} absorption is due to the antisymmetric combination of the intrafragment CC stretching of each fragment's central CC bond, which becomes allowed and gains intensity due to electron-vibrational coupling.[3]

The solid state UV-visible spectrum of $[Et_4N]_2[TCNE]_2$ has two broad bands at 26150 cm^{-1} (382 nm; 3.24 eV) as well as a new absorption at 16850 cm^{-1} (593 nm; 2.09 eV) (Fig. 3). The latter absorption is assigned to the dimer (to a $b_{2u}{}^2b_{1g}{}^0$ ($^1A_{1g}$) $\rightarrow$ $b_{2u}{}^1b_{1g}{}^1$ ($^1B_{1u}$) transition, see below), and gives these dimers their observed dark blue-purple color. This value is higher in energy than the 15300 cm^{-1} (654 nm, 1.90 eV) reported for $Tl_2[TCNE]_2$, $[(Me_2N)_2CC(NMe_2)_2][TCNE]_2$, and $[Cr^I(C_6H_6)]_2[TCNE]_2$.[2]

Finally, when π-$[TCNE]_2^{2-}$ dimers are present, there is a change in the magnetic properties of the dimerized solid and, as noted for related π-$[TCNE]_2^{2-}$ dimers, diamagnetic-like behavior is observed for $[Et_4N]_2[TCNE]_2$.[1]

The changes in the IR and UV-visible spectra, magnetic behavior, and structure are in accord with those expected if a bond existed within the $[TCNE]^-$ fragments, which form the π-$[TCNE]_2^{2-}$ dimers. However, anions are expected to be repulsive when isolated. So, how do we explain the existence of bonding interactions in π-$[TCNE]_2^{2-}$ dimers?

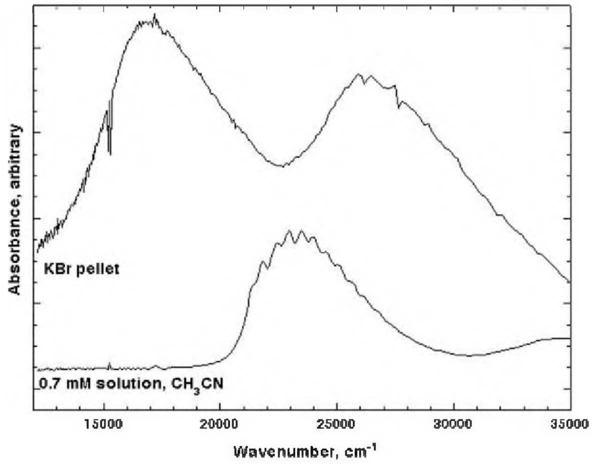

Fig. 3 Solid state UV-visible spectra of $[TCNE]_2^{2-}$ in a KBr pellet of $[Et_4N]_2[TCNE]_2$, and in a low concentration solution of CH_3CN, where only $[TCNE]^{\bullet-}$ exists.[1]

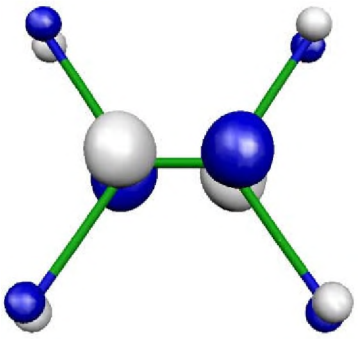

Fig. 4 Shape of the SOMO orbital of the $[TCNE]^{\bullet-}$ radical as indicated by the isosurfaces of 0.001 au. Zones in blue indicate positive regions, while red zones refer to negative ones.

3. The nature of the interactions between anionic radicals

Following Pauling,[4] we accept here that, "…there is a chemical bond between two atoms or groups of atoms in the case that the forces acting between them are such as to lead to an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species." Therefore, we have to start by looking at the energetics of the $[TCNE]^- \cdots [TCNE]^-$ interaction to define whether a bond can be present between the two fragments of the π-$[TCNE]_2^{2-}$ dimers.

What are the energetics of these π-$[TCNE]_2^{2-}$ dimers? The $[TCNE]^{\bullet-}$ fragments present a dual nature of anion and radical (the electronic structure of $[TCNE]^{\bullet-}$ has an open shell SOMO, see Fig. 4, which confers a radical nature to the anion). Looking only at the anionic nature of the $[TCNE]^{\bullet-}$ fragments, simple electrostatics indicates that the fragments of the dimer should be repulsive. On the other hand, as for any other radical, the unpaired electrons tend to form covalent bonds between the radicals. Summarizing, there are two interactions of opposite sign between a pair of $[TCNE]^-$ radical anions: a repulsive Coulombic (E_{coul}) component, induced by the anionic character of the $[TCNE]^-$ monomers, and an attractive (E_{bond}) bonding component, induced by the radical character of the $[TCNE]^-$ monomers. The dimers are not energetically stable for $E_{coul} \gg E_{bond}$, but if $E_{coul} \ll E_{bond}$ there is a stable minimum for the dimers, which thus become energetically stable species. As shown in Fig. 5, there is a smooth transition between these two extreme situations as the relative importance of the E_{bond} component increases relative to E_{coul}. If E_{bond} is negligible compared to E_{coul}, obviously $E_{int} = E_{coul}$ (upper red curve in Fig. 5). As E_{bond} increases relative to E_{coul}, a local minimum above the energy of dissociation into two $[TCNE]^-$ monomers occurs, that is, the dimer becomes a metastable species (higher two violet curves in Fig. 5). The barrier towards dissociation of this local minimum lowers as the importance of E_{bond} increases, until it disappears when $E_{bond} > E_{coul}$ at all distances between the fragments (lowest energy violet curve in Fig. 5). The local minimum becomes a global minimum when its energy is more stable than the dissociated $[TCNE]^-$ monomers (see the lowest two green curves in Fig. 5). Depending on the shape of the E_{bond} curve, this can happen before the barrier disappears (as in the upper green curve in Fig. 5).

Ab initio RB3LYP calculations performed by us at various levels[2] have shown that the energy of the isolated dimers at the geometry of the reported crystal structures lies above that of two dissociated $[TCNE]^-$ monomers (Fig. 6). The two potential energy curves of Fig. 6 show a higher energy metastable minimum at short C–C distances, which corresponds to the formation of a $[C_4(CN)_8]^{2-}$ monomer, while another metastable minimum is found at lower energies for the π-$[TCNE]_2^{2-}$ dimers. So the computed curves can be associated

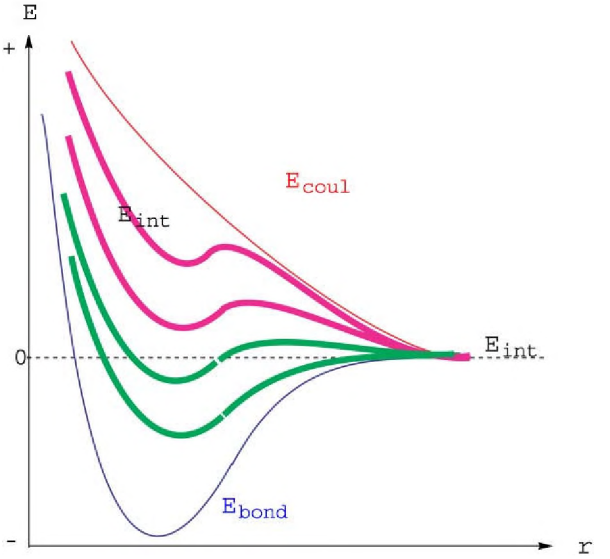

Fig. 5 Schematic potential energy curves (bold violet curves) obtained by combining an attractive (E_{coul}, red) and repulsive (E_{bond}, blue) energetic components. The upper two curves show the presence of local metastable minima, while the lowest one only shows an absolute minimum.

to either of the violet curves depicted in Fig. 5. However, no minimum is found for the π-$[TCNE]^-$ dimers at the UHF, UB3LYP or MCSCF levels, thus indicating that the dimer found for the π-$[TCNE]_2^{2-}$ dimers in Fig. 6 is a spurious consequence of the imposition of double occupancy present in the RB3LYP method. In conclusion, as a minimum is found between the monomers of the π-$[TCNE]_2^{2-}$ dimers when they are isolated, we conclude that *no bond is found in the isolated π-$[TCNE]_2^{2-}$ dimers in the gas phase*.

The mere presence of π-$[TCNE]_2^{2-}$ dimers at an average C–C interfragment distance of 2.9 Å indicates that the situation in the crystals is more complex than in the isolated dimer. We analyze the energetics of π-$[TCNE]_2^{2-}$ dimers by studying the $[Et_4N]_2[TCNE]_2$ crystal, where these dimers have an intradimer distance of 2.827 Å. This can be done by computing the interaction energy between all pairs of molecules in the $[NEt_4]_2[TCNE]_2$ aggregate, Fig. 1. At the UHF/6-31+G(2d,2p) level the $[TCNE]^-\cdots[TCNE]^-$ interaction energy is repulsive by 83.5 kcal mol^{-1}, while the $[NEt_4]^+\cdots[NEt_4]^+$interaction is repulsive by 19.3 kcal mol^{-1}. In contrast, the four different $[NEt_4]^+\cdots[TCNE]^-$ interactions are all attractive (by −58.1, −58.0, −66.1, and −66.0 kcal mol^{-1}). Consequently, the $[NEt_4]_2[TCNE]_2$aggregate has an overall stabilization energy of −145.2 kcal mol^{-1} (*i.e.*, 145.2 kcal mol^{-1} is required to dissociate $[NEt_4]_2[TCNE]_2$ into two $[TCNE]^-$ and two $[NEt_4]^+$ ions). Thus, as in any conventional ionic crystal (like rock salt) the cation···anion interactions are capable of overcompensating the cation···cation and anion···anion repulsions, and stabilize formation of π-$[TCNE]_2^{2-}$ dimers within the crystal.[5]

What happens when the ionic cation···anion interactions force the two open shell anions to be close together? *Ab initio* B3LYP/6-31+G(2d,2p) calculations on the isolated π-$[TCNE]_2^{2-}$ dimer or on the $[NEt_4]_2[TCNE]_2$ aggregate of Fig. 1, indicate that the electronic structure of the dimer (see Fig. 7) is similar to that found when the interaction is energetically stabilizing (in other words, gives rise to the formation of a bond between the fragments). The short anion···anion distance induced by the cation···anion interaction, allows the overlap of the b_{2g} SOMO orbitals of the fragments, giving rise to the formation of a b_{2u} bonding and a b_{1g} antibonding dimer orbital (the bonding combination is

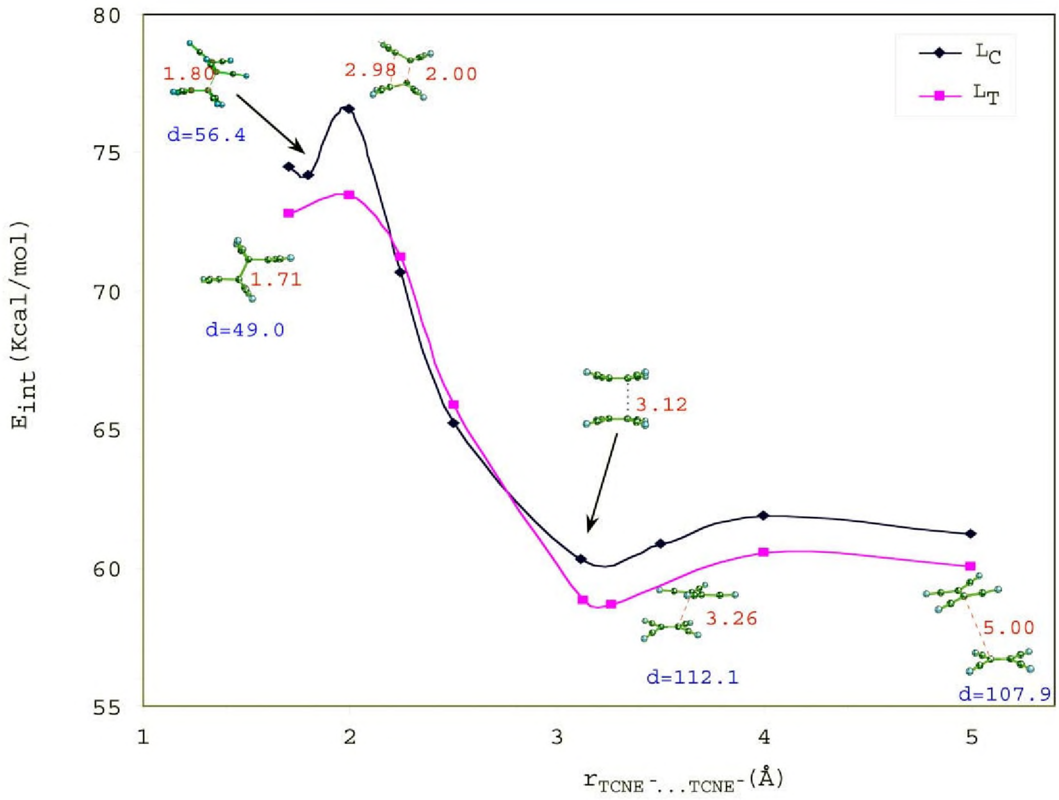

Fig. 6 Variation with distance of the interaction energy between two $[TCNE]^{\bullet -}$ monomers (calculated at the RB3LYP/6-31+G level). The geometry of the dimers was optimized at each fixed distance.[2a] The curve was computed for the L_C and L_T conformers found experimentally (see ref. 2 for details).

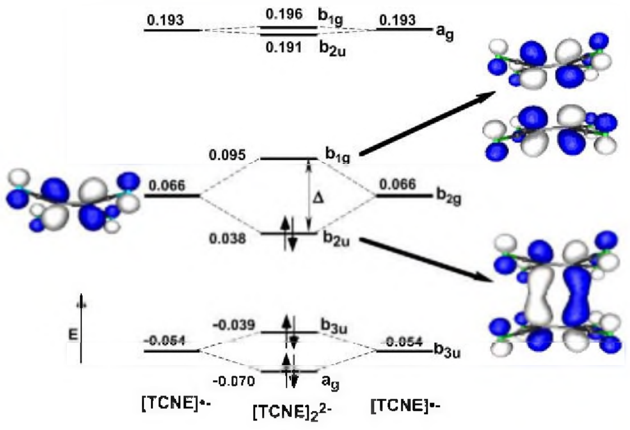

Fig. 7 Shapes of the π-[TCNE]$_2^{2-}$ dimer orbitals generated from the HOMO, SOMO and LUMO orbitals of the [TCNE]$^{\cdot-}$ fragments. The energies are in atomic units (au; 1 au = 627.51 kcal mol^{-1}). The results are from a B3LYP/6-31+G(2d,2p) calculation at the crystal geometry of the dimer.

lower in energy and becomes the LUMO if the dimer is a singlet). The two orbitals are separated by a energy increment Δ proportional to the overlap. This electronic structure is the same as expected for the interaction of an isoelectronic neutral radical.

At an intradimer separation of 2.8 to 3.5 Å, Δ is large, and the most stable form of placing the two electrons in the b_{2u} and b_{1g} orbitals is the diamagnetic one shown in Fig. 7. This agrees well with the experimental diamagnetic nature of the dimer. The presence of Δ also explains the existence of a new electronic absorption that occurs at 16850 cm^{-1}. *Ab initio* calculations on the dimer confirm the assignment of the IR bands observed above and the presence of new bands associated with the dimer.

What name do we assign to the interaction found in some ionic crystals between the fragments of the π-[TCNE]$_2^{2-}$ dimer? There is no previous experience of a similar type of compound, so we have to extrapolate from conventional compounds. The interplay between attractive (E_{bond}) and repulsive (E_{coul}) components of the interaction complicates the extrapolation. The fact that the π-[TCNE]$_2^{2-}$ dimer shares the electronic structure of a conventional bond and also the stability, when the cations are considered, suggest that one can think of a form of supramolecular cation-induced and stabilized anion···anion interaction. It is consistent with previous knowledge to call this interaction a cation-induced bond. Although it originates from the same electronic principles, this bond is not conventional in two aspects: (a) it involves the presence of a third body (the cation), and (b) it is much weaker and at larger distances that the conventional covalent C–C bonds (a fact that originates from the anion···anion repulsion). A topological analysis of the electron density of the B3LYP/6-31+G(2d,2p) wavefunction using Bader's methodology[6] also shows that this new bond is of the C–C type. Two (3,−1) bond critical points, linking one C atom from each [TCNE]$^-$ unit, were found. The characteristic of these critical points are in the range of values found in intermolecular bonds: the electron density is 0.012, the Laplacian 0.023, and the $|\lambda_1|/\lambda_3$ ratio 0.201, all values in atomic units. Thus, we refer to it as being a *cation-mediated supramolecular C–C bond*.

One can argue about the use of the term bond, as the direct anion···anion interaction is not energetically stabilizing. Thus, some authors have suggested the use of the term "bonding interaction" for these unconventional bonds (because of their strength and their equilibrium distance), but this is inappropriate for the following three reasons: (a) it is an artifactual division of the bonds, based on their energy and distance, (b) the limits where such a term should be used are not clear-cut, and (c) it de-emphasizes the bonding found experimentally and theoretically. Also, according to Pauling,[4] any bonding interaction is a bond. Thus, a "long C–C bond" is more appropriate to describe the properties of this new type of bond.

4. When should [TCNE]$_2^{2-}$ dimers exist?

The previous discussion has shown that the two-electron four-centered intradimer bond between two [TCNE]$^-$ fragments is due to (1) the radical nature of the fragments, which allow the formation of a new bond, and (2) the presence of cation–anion interactions, which provide electrostatic stabilization enabling the radical anions to get close to each other, and allowing orbital overlap of each fragment (the electronic mechanism behind this interaction). Consequently, it is possible that a different polymorph of [Et$_4$N]$_2$[TCNE]$_2$ exists that does not exhibit the cation-induced intradimer C–C bond formation. Whenever these two factors are significant, as can be expected for all charged radicals, one can expect similar behavior.

Finally, we note that cation-induced bond formation must not be confused with van der Waals bond formation. Van der Waals' bonds require two closed shell fragments, with no charge or dipole in them, as the dominant energetic term is the so-called dispersion, whose origin relies on the instantaneous dipoles of the electrons (in a classical view of the problem). The bond described herein is also not a typical ionic bond, as those bonds do not present the E_{bond} term associated with the radical nature of the fragments. However, the electrostatic term is the dominant one in the interaction, as our calculations have shown.

5. Computational details

Ab initio UB3LYP/6-31+G(2d,2p) computations were carried out using the non-local B3LYP exchange and correlation DFT functional[7] and the 6-31+G(2d,2p) basis set, using a determinant in which the orbitals are not restricted to be doubly occupied. All the computations were carried out using the Gaussian-98 suite of programs.[8] The critical point analysis was done using the AIMPAC package.[9]

Acknowledgements

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