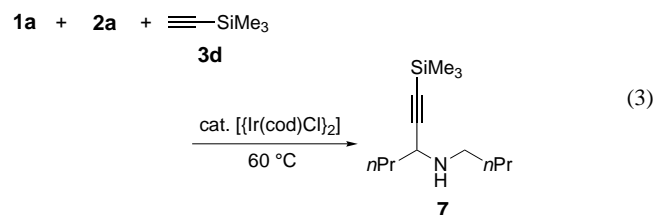The reaction of **1a**, **2a**, and trimethylsilylacetylene (**3d**) under the influence of [{Ir(cod)Cl}$_2$] afforded an adduct, butyl(1-propyl-3-trimethylsily-2-propynyl)amine [**7**; Eq. (3)].

$$\textbf{1a} \ + \ \textbf{2a} \ + \ \equiv\!\!-\!\!SiMe_3$$
$$\textbf{3d}$$

(3)

Here the the alkyne **3d** has added to the double bond of the imine **5a** initially formed, in contrast to the reaction of the aliphatic alkyne **3a**. It is probable that the reaction proceeds through the oxidative addition of the Ir^I complex to the terminal C−H bond of alkyne **3d**, followed by insertion of the imine to the resulting Ir−H complex. Recently, Miyaura et al. reported that the iridium-catalyzed dimerization of terminal alkynes involves the oxidative addition of a low-valent Ir complex to alkyne, followed by insertion of an alternative alkyne to give dimers.[9]

In summary, we have developed a new reaction of aldehydes, amines, and alkynes catalyzed by an Ir complex to produce three-component coupling products. These products are difficult to obtain by conventional organic synthetic methods.

Experimental Section

Representative procedure: The aldehyde (0.5 mmol), amine (0.25 mmol), and alkyne (0.5 mmol) were added under Ar to a solution of [{Ir(cod)Cl}$_2$] (0.025 mmol) in THF (2.0 mL). Then the reaction mixture was stirred at 60 °C for 15 h. The reaction was quenched with wet Et$_2$O, and the products were isolated by column chromatography (230 – 400 mesh Al$_2$O$_3$, hexane) and purified by distillation under reduced presure. After the reaction, GC and GC-MS analyses were performed. The yields of the products were estimated from the peak areas based on the internal standard technique using GC.

4a: ^{1}H NMR: $\delta = 7.59$ (t, $J = 4.9$ Hz, 1H), 4.91 (s, 1H), 4.76 (d, $J = 1.3$ Hz, 1H), 3.41 (t, $J = 6.9$ Hz, 1H), 2.25 (dt, $J = 5.3$, 7.3 Hz, 2H), 2.04 (t, $J = 7.3$ Hz, 2H), 1.65 – 1.09 (m, 14H), 0.95 (t, $J = 7.6$ Hz, 3H), 0.88 (t, $J = 4.6$ Hz, 6H); ^{13}C NMR: $\delta = 163.8$, 151.7, 108.9, 76.0, 37.6, 36.7, 32.5, 31.7, 29.1, 27.7, 22.5, 19.6, 14.0, 13.8, 13.7; IR (neat) 2957, 1667, 1462, 897 cm^{-1}; MS (70 ev) m/z (%): 237 (0.3) [M^+], 194 (100), 180 (5), 166 (16).

7: ^{1}H NMR: $\delta = 3.35$ (dd, $J = 7.7$, 5.9 Hz, 1H), 2.84 (ddd, $J = 6.6$, 8.4, 11.4 Hz, 1H), 2.56 (ddd, $J = 5.9$, 8.0, 11.4 Hz, 1H), 1.61 – 1.33 (m, 8H), 0.94 (t, $J = 7.3$ Hz, 3H), 0.91 (t, $J = 7.3$ Hz, 3H), 0.16 (s, 9H); ^{13}C NMR: $\delta = 100.2$, 87.3, 50.6, 47.0, 38.0, 32.1, 20.4, 19.2, 13.9, 13.8, 0.1; IR (neat) 3299, 2959, 2159, 1458, 1243, 842 cm^{-1}; MS (70 ev) m/z (%): 182 (100), 109 (4), 73 (12).

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Unprecedented Detection of Distinct Barriers Involving Formally Enantiotopic Substituents: Phenyl Rotation in Solid Diphenyl Sulfoxide**

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It has been pointed out that "the vast majority of molecules are chiral, not achiral; to realize it, one only needs a sufficiently fine spatial or temporal resolution of measurement".[2] To illustrate this point herein, we refer to the recent observation that dimesityl sulfoxide (Mes$_2$S=O; Mes = 2,4,6-trimethylphenyl), which by convention is an achiral molecule

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(C_s point group by virtue of the symmetry plane created by the fast Mes−SO rotation), appears chiral in the crystalline state.[1a] This is a consequence of the two mesityl rings adopting a propellerlike conformation, which deprives the molecule of its symmetry plane: the "static" molecule thus belongs to the C_1 point group. For this reason the solid-state ¹³C cross-polarization magic-angle-spinning (CP-MAS) NMR spectrum at ambient temperature displays anisochronous lines for the methyl substituents:[1a] the two rings, in fact, are not symmetry related and are therefore diastereotopic. The same situation is observed in solution,[1a] as shown by the NMR spectra taken at a temperature (−177 °C) low enough to "freeze" the Mes−SO rotation that makes the molecule apparently achiral.

Like dimesityl sulfoxide, diphenyl sulfoxide is achiral under conditions of fast rotation about the Ph−SO bond but, contrary to dimesityl sulfoxide, is achiral also in its ground state conformation, since the plane of symmetry is maintained even when the Ph−SO rotation is blocked. Molecular mechanics calculations[3] show (Figure 1) that both the Ph−SO

(Figure 1); the difference with respect to the calculated values are a result of the flattening effect of the lattice. (Computation[6] and X-ray diffraction[7] studies indicate that benzophenone, in which the SO has been replaced by a CO group, maintains the same propellerlike structure as its more hindered analogue, dimesityl ketone, at variance with the behavior of diphenyl sulfoxide with respect to dimesityl sulfoxide.)

The crystal space group $P2_1/n$ of diphenyl sulfoxide has a center but does not have a plane of symmetry, whereas the molecule has a plane but not a center of symmetry (site symmetry different from molecular symmetry), so that the two phenyl rings reside in two different spatial environments and are therefore diastereotopic. Accordingly, the solid-state ¹³C CP-MAS NMR spectrum at −30 °C displays anisochronous signals for the carbon atoms of one ring with respect to those of the other.

As shown in Figure 2c two lines each are observed for the quaternary as well for the para carbon atoms, and three lines (1:1:2) were assigned to four ortho carbon atoms.[8] The four
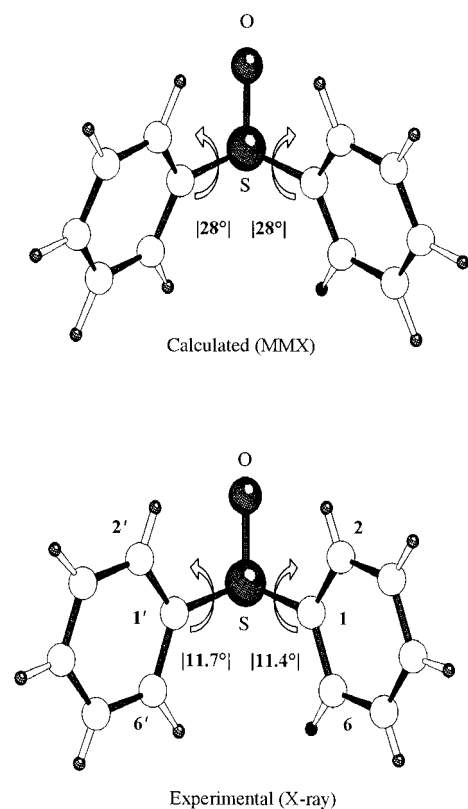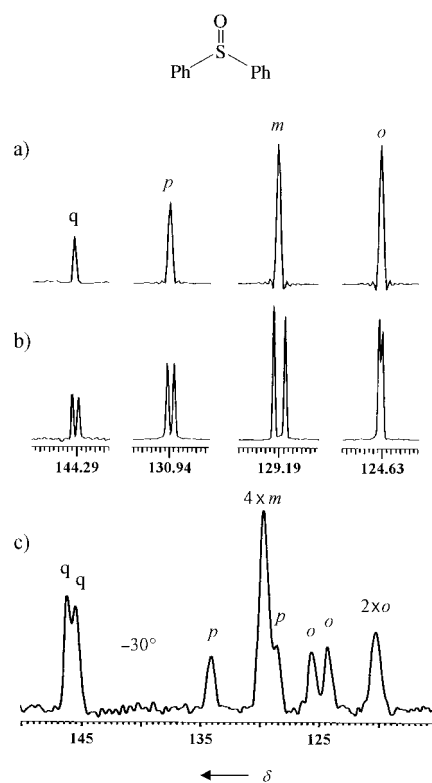

Figure 1. Computed structure (MMX force field[3]) of diphenyl sulfoxide (top). Underneath is reported the structure obtained by X-ray diffraction.

dihedral angles have equal absolute values (28°), thus leading to a symmetric butterflylike shape (C_s point group), at variance with the propellerlike conformation (C_1 point group) of dimesityl sulfoxide.[4] Diphenyl sulfoxide also adopts a butterflylike conformation in the crystalline state, as shown by X-ray diffraction studies (see Experimental Section) of a single crystal in which the two Ph−SO dihedral angles appear to coincide (11.7° and 11.4°)[5] within experimental error

Figure 2. a) ¹³C NMR (100.6 MHz) spectrum of diphenyl sulfoxide in a solution of CDCl₃ at ambient temperature: the quaternary, para, meta, and ortho carbon atoms are labeled as q, p, m, and o, respectively. b) The same spectrum (100.6 MHz) taken at ambient temperature in a chiral environment:[16] the splitting of the lines cover the range 0.8 Hz (ortho carbon atoms) – 2.7 Hz (meta carbon atoms). c) Static ¹³C NMR (75.45 MHz) CP-MAS spectrum of solid diphenyl sulfoxide at −30 °C.

meta carbon atoms yield a single signal, owing to a fortuitous coincidence of the corresponding lines. The line-shape simulation (Figure 3, bottom right) indicates that the ortho line with double intensity actually comprises two different peaks with a separation (15 Hz) smaller than the line width
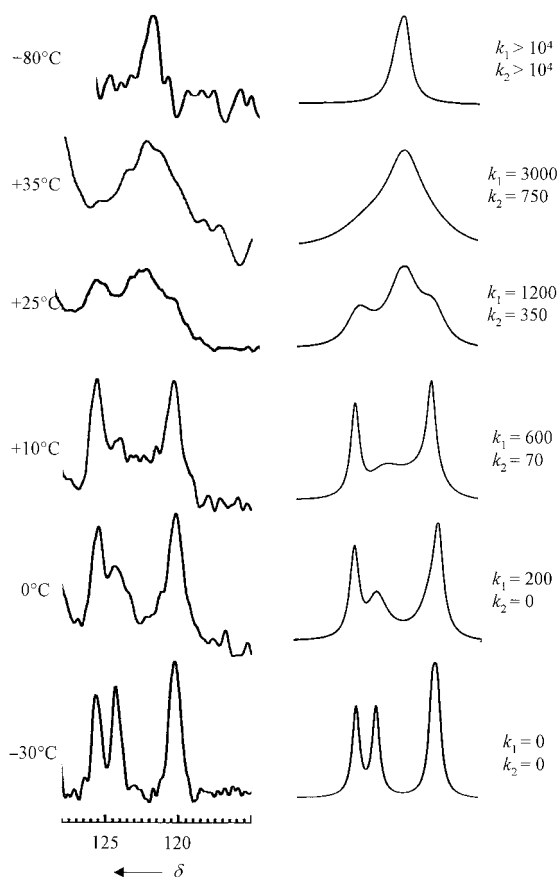
Figure 3. Dynamic solid-state ^{13}C NMR spectrum (75.45 MHz) of the *ortho* carbon atoms of diphenyl sulfoxide as a function of temperature (left). On the right is displayed the computer simulation obtained with the pairs of rate constants (k_1 and k_2 in s^{-1}) reported.

(27 Hz), thus explaining why its height is less than twice the height of the other two signals. There are therefore four anisochronous signals (two for each phenyl group) related to the four *ortho* carbon atoms of the static molecule,[9] as expected on the basis of a blocked rotation about the Ph—SO bonds[10] coexisting with different site and molecular symmetries.

The anisochronous signals observed at $-30\,°C$ in the ^{13}C NMR spectrum of crystalline diphenyl sulfoxide are a consequence of the sulfur atom being a prochiral tetrahedral center[11] with two enantiotopic ligands in the isolated molecule.[11–14] For this reason the situation encountered in the crystal is similar (although not identical) to that occurring in a fluid chiral medium in that "enantiotopic groups exhibit their distinctiveness only in a chiral extramolecular environment".[12] Actually, the four ^{13}C NMR spectral lines (which correspond to four heterotopic ring carbon atoms) observed in an achiral solution (Figure 2a), split into pairs[15] (Figure 2b) when the spectrum is taken in a chiral environment:[16] here the two phenyl groups become diastereotopic and consequently give rise to anisochronous signals. The difference between the situation in the crystal and that in solution is because of the fact that to convert two enantiotopic into diastereotopic ligands, it is not strictly necessary to have a chiral extramolecular environment: a more general requirement should actually state that it is sufficient to have the

element of symmetry of the external environment not coincident with that of the molecule. For instance the $P2_1/n$ space group, which has a center of symmetry, is not chiral (as is the Pirkle alcohol[16] employed to obtain the spectrum of Figure 2b), yet the solid-state spectral lines are anisochronous because, when such a situation occurs, the arrangement of the molecules embedded in the crystal packing gives rise, in practice, to a chiral object, thus rendering diastereotopic the ligands that are enantiotopic when the molecule is considered isolated from its environment. In the situation encountered here the two phenyl groups of diphenyl sulfoxide should thus display differences in all their observable features, and such a distinctiveness should include not only the static but also the dynamic properties. However, the chances of the latter differences becoming experimentally detectable are likely to be very low. This explains why, to the best of our knowledge, distinct dynamic effects have not been reported for any molecule that should have exhibited such features, that is, one with a structure and symmetry analogous to that of an achiral sulfoxide. A rare event, however, can occasionally be discovered in a serendipitous way and indeed it was by sheer chance that we found such evidence in the present case.

On raising the temperature of the diphenyl sulfoxide solid-state spectrum above $-30\,°C$, the lines for the *ortho* carbon atoms broaden significantly and subsequently coalesce, ultimately displaying a single signal above ambient temperature (Figure 3). This feature is a result of the Ph—SO rotation process exchanging the *ortho* positions[17] (the occurrence of dynamic NMR spectroscopy effects in the crystalline state is well documented[18]). On the contrary, the signals of the quaternary and *para* carbon atoms remain sharp, because they lie in the local rotation axis and do not experience the effects of the exchange process.[19] Likewise, the signal for the *meta* carbon atoms remains sharp, owing to the coincidental overlap of the corresponding lines.

An interesting feature was however observed: when the inner pair of lines corresponding to the *ortho* carbon atoms begin to broaden, the outer lines remain sharp, and when the inner lines coalesce, the outer lines are broadened but still separated. Likewise when the outer lines reach their coalescence temperature, the inner lines have already merged into a single peak. These observations suggest that one of the two rings rotates faster than the other, which means that there are two free energies of activation for two distinguishable rotation processes.

This was proven in a quantitative way by the line-shape simulation[20] displayed in Figure 3, which allowed the values of the two rate constants to be determined at various temperatures.[21] Even if the absolute temperatures are in error of a few degrees, this does not affect the difference in the k values, since each pair of these rate constants was determined at exactly the same temperature. Thus, for example, at $0\,°C$ (Figure 3) one ring makes 200 ± 40 rotations per second, whereas the other is essentially static, as it has a negligible rotation rate. The two free energies of activation ($\Delta G^{\pm}$) derived from the two sets of rate constants[22] differ by $1.0 \pm 0.2\ \mathrm{kcal\,mol^{-1}}$, and their absolute values are 14.0 and 13.0 kcal mol^{-1}. The temperatures where different rate constants (k_1 and k_2 values) could be identified encompass,
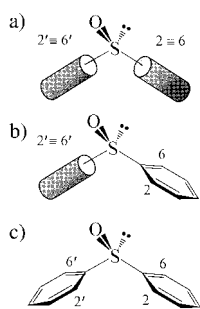
Scheme 1. Pictorial representation of the time averaged shape of crystalline Ph_2SO as function of the two distinct rotation rates about the Ph−SO bonds.

approximately, the $-10°$ to $+35°C$ range. At even higher temperatures, the two rotation rates are still expected to be different, but such a difference cannot be measured anymore by the NMR spectroscopy technique: for instance, the spectrum at $+80°C$ in Figure 3 could be simulated with two essentially equal rate constants.

To give an approximate image of the effect illustrated here, the phenyl rings were drawn (Scheme 1a) as hexagons to indicate the static situation at low temperature. At the temperature when the rotation of one ring is slow and that of the other is fast in the NMR time-scale (about $0°C$), the rotating ring was drawn as a cylinder (Scheme 1b) where the ortho positions 2′ and 6′ interchange rapidly, whereas the motionless ring is still drawn as a hexagon. Finally, both phenyl groups were drawn (Scheme 1c) as cylinders (where both the pairs 2,6 and 2′,6′ are scrambled) to symbolize their fast rotation at higher temperatures.

In conclusion, distinctive stereodynamic processes that involve the two enantiotopic substituents of a formally achiral molecule (e.g. diphenyl sulfoxide) can be observed only in situations where the anisotropic environment (in this case the crystal packing) renders the two groups symmetry nonequivalent, thus making the whole supramolecular system chiral; on the contrary this effect cannot be detected in achiral isotropic media, unless the formally achiral molecule adopts a chiral conformation.[23]

Experimental Section

X-ray diffraction—Crystal Data of Diphenyl sulfoxide: $C_{12}H_{10}OS$ (202.26), monoclinic, space group $P2_1/n$, $Z = 4$, $a = 8.3490(3)$, $b = 14.0970(5)$, $c = 8.9170(3)$ Å, $\beta = 101.1150(10)$, $V = 1029.81(6)$ Å^3, $D_c = 1.305$ g cm^{-3}, $F(000) = 424$, $\mu M_o = 0.275$ cm^{-1}, $T = 293$ K. Data were collected using a graphite monochromated Mo$_{K\alpha}$ X-radiation ($\lambda = 0.71073$ Å) range $2.74° < \theta < 35.00°$. Of 18196 reflections measured, 4533 were found to be independent ($R_{int} = 0.0324$), 2696 of which were considered as observed [$I > 2\sigma(I)$], and were used in the refinement of 103 parameters leading to a final R_1 of 0.0496 and a R_{all} of 0.0764. The structure was solved by direct methods and refined by full-matrix least squares on F^2, using SHELXTL 97 program packages. In refinements were used weights according to the Scheme $w = [\sigma^2(F_o^2) + (0.1007P)^2 + 0.0000P]^{-1}$, where $P = (F_o^2) + 2 F_c^2)/3$. The phenyl rings were assumed to be regular hexagons, the hydrogen atoms were located by geometrical calculations and refined by using a "riding" method; $wR_2 = 0.1727$. The goodness-of-fit parameter S was 1.023. Largest difference between peak and hole was 0.283 and -0.283 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156961. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc. cam.ac.uk).

NMR measurements: The ^{13}C NMR solution spectra were obtained at 100.6 MHz (Varian, Mercury) and the ^{13}C NMR solid-state CP-MAS spectra at 75.45 MHz (Bruker CXP spectrometer). For the latter measurements, solid diphenyl sulfoxide (the same batch from which the crystal for X-ray diffraction had been selected) was introduced into a tightly sealed 7-mm zirconia rotor, and spun at the magic angle with a speed of about

3.5 KHz. The chemical shifts were measured with respect to the lower frequency signal of the adamantane ($\delta = 29.4$ ppm). The assignment of the CH carbon atoms was obtained by the "nonquaternary suppression" pulse sequence. The signals for the ortho and meta carbon atoms were assigned by comparison with those of the solution spectrum. In $CDCl_3$, the two lines assigned to four carbon atoms at $\delta = 129.2$ and 124.6 correspond to the single line at $\delta = 129.4$ and to the average position ($\delta = 122.5$) of the four exchanging lines of the solid-state spectrum, respectively. When the ^{13}C solution spectrum is obtained in the undecoupled mode, the line at $\delta = 129.2$ displays long-range coupling to a single hydrogen atom, and the signal at $\delta = 124.6$ shows long-range coupling to two hydrogen atoms. Therefore, the former is unambiguously assigned to a meta and the latter to an ortho carbon atom.[24] Cooling was achieved by means of a flow of dry nitrogen, precooled in a heat exchanger immersed in liquid nitrogen. The temperatures of the solid-state spectra were calibrated by using the shift dependence of the ^{13}C lines of 2-chlorobutane absorbed on solid decalite,[25] assuming a dependence equal to that observed in neat liquid, which had been previously calibrated by using a Ni/Cu thermocouple.

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[2] H. Zabrodsky, D. Avnir, *J. Am. Chem. Soc.* **1995**, *117*, 462; see also: D. Avnir, O. Katzenelson, H. Zabrodsky Hel-Or, *Chem. Eur. J.* **1996**, *2*, 744.

[3] MMX force field as implemented in the computer package PC Model, Serena Software, Bloomington, IN, USA.

[4] The Ar−SO dihedral angles of dimesitylsulfoxide were calculated[1a] to be equal to $+107°$ and $-9°$ (MMX force field). In the analogous hindered 2,2′,6,6′-tetramethyldiphenyl sulfoxide, the experimental values for these angles were $+113°$ and $-9°$ (X-ray diffraction).[1a]

[5] These are the absolute values of the dihedral angles O-S-C1-C2 and O-S-C1′-C2′, respectively (Figure 1), and are in good agreement with those (11.8° and 10.9°) obtained from the X-ray data reported in: A. V. Yatsenko, S. V. Medvedev, A. I. Tursina, L. A. Aslanov, *Zh. Obs. Khim.* **1986**, *56*, 2330.

[6] R. J. Abraham, I. S. Haworth, *J. Chem. Soc. Perkin Trans. 2* **1988**, 1429.

[7] E. B. Fleischer, N. Sung, S. Hawkinson, *J. Phys. Chem.* **1968**, *72*, 4311.

[8] The chemical shifts of the 75.45-MHz CP-MAS ^{13}C NMR spectrum (Figure 2c) are: $\delta = 146.1$ (q), $\delta = 145.35$ (q), $\delta = 134.0$ (p), $\delta = 129.4$ (4 × m), $\delta = 128.5$ (p), $\delta = 125.6$ (o), $\delta = 124.2$ (o), $\delta = 120.2$ (2 × o). Line-shape simulation (Figure 2) shows that the latter signal is the combination of two lines at $\delta = 120.3$ and 120.1.

[9] The assignment of the signals to the meta and ortho carbon atoms was performed as described in the Experimental Section. Such an assignment is, however, immaterial for what concerns the dynamic process; the conclusion would be the same even if signals for the meta and ortho carbon atoms were identified incorrectly.

[10] Such a restricted rotation was observed in solution, even at the lowest attained temperature (about $-175°C$), in agreement with MM calculations,[3] which predict a barrier as low as 1.6 kcalmol^{-1} for the independent Ph−SO rotation in the isolated molecule. Clearly, the crystal lattice imposes additional restrictions on the motion that renders the transition-state energy higher than in solution, thereby allowing detection of the dynamic process by CP-MAS NMR spectroscopy. An increase in the barriers to internal motions in the solid state with respect to solution has been reported in a number of cases (see ref. [18]).

[11] K. R. Hanson, *J. Am. Chem.Soc.* **1966**, *88*, 2731.

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[13] W. B. Jennings, *Chem. Rev.* **1975**, *75*, 307.

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[15] The fast Ph−SO bond rotation that still occurs in the chiral solution makes the ortho carbon atoms (C-2 ≡ C-6 and C-2′ ≡ C-6′) give rise to two (Figure 2b) rather than four lines (Figure 2c). The Ph−SO rotation in the crystal at $-30°C$ is frozen in the NMR time-scale, so that within each of the two phenyl groups, the ortho positions are syn or anti to the oxygen atom (C-2 ≢ C-6 and C-2′ ≢ C-6′).

[16] The chiral environment was obtained by the addition an appropriate amount of enantiopure (*R*)-(−)-1-(9-anthryl)-2,2,2,-trifluoroethanol to a CDCl$_3$ solution (see: W. H. Pirkle, *J. Am. Chem. Soc.* **1966**, *88*, 1837).

[17] Under conditions of fast exchange, two averaged lines should actually be observable, one for each pair of *ortho* carbon atoms of the two rapidly rotating phenyl groups. However, the separation of these two averaged lines ($\Delta\delta = 0.6$) is too small to be resolved, as also shown by the computer line-shape simulation (see Figure 3).

[18] F. G. Riddell, S. Arumagam, J. E. Anderson, *J. Chem. Soc. Chem. Commun.* **1991**, 1525; P. J. Barrie, J. E. Anderson, *J. Chem. Soc. Perkin Trans. 2* **1992**, 2031; F. G. Riddell, S. Arumagam, K. D. M. Harris, M. Rogerson, J. H. Strange, *J. Am. Chem. Soc.* **1993**, *115*, 1881; A. E. Aliev, K. D. M. Harris, D. C. Apperley, *J. Chem. Soc. Chem. Commun.* **1993**, 251; F. G. Riddell, G. Bernath, F. Fülöp, *J. Am. Chem. Soc.* **1995**, *117*, 2327; D. Casarini, L. Lunazzi, A. Mazzanti, *J. Org. Chem.* **1998**, *63*, 9125; L. Lunazzi, A. Mazzanti, D. Casarini, O. De Lucchi, F. Fabris, *J. Org. Chem.* **2000**, *65*, 883; J. E. Anderson, D. Casarini, L. Lunazzi, A. Mazzanti, *J. Org. Chem.* **2000**, *65*, 1729; D. Casarini, L. Lunazzi, A. Mazzanti, G. Simon, *J. Org. Chem.* **2000**, *65*, 3207.

[19] This feature guarantees that the observed dynamic process cannot be caused by a 180° rotation of the whole molecule within the crystal, leading to an exchange of the positions of the two phenyl groups. In this case, the signals of the quaternary and *para* carbon atoms should also have displayed line-broadening effects, as observed with the signals for the *ortho* carbon atoms.

[20] Use was made of a PC version of the DNMR6 computer program n° 633 of QCPE, Indiana University, Bloomington, IN, USA.

[21] The shift separation between the inner pair of lines ($\Delta\delta = 3.9$) is too close to that between the outer pair ($\Delta\delta = 5.5$)[8] to account for the observed line shape on the basis of a unique free energy of activation, as clearly demonstrated by the computer simulation. When the two rings were assumed to have identical rotation rates (i.e. coincident ΔG^{+} values), it was impossible to reproduce the experimental dynamic spectra of Figure 3.

[22] As is usually observed in rotation processes, in the present experiment the ΔG^{+} values were found also to be independent of temperature, which indicates a negligible value for the corresponding ΔS^{+}; see: D. Casarini, L. Lunazzi, E. Foresti, D. Macciantelli, *J. Org. Chem.* **1994**, *59*, 4637.

[23] An example of this type is provided by the two different rotation barriers measured for the *tert*-butyl substituents in (*t*Bu)$_2$CH(*i*Pr), owing to the molecule adopting a chiral conformation when the CH−*i*Pr bond rotation is frozen (J. E. Anderson, B. R. Bettels, H. M. R. Hoffman, P. Pauluth, S. Hellmann, H. D. Beckhaus, C. Ruchardt, *Tetrahedron* **1988**, *44*, 3701).

[24] F. W. Wehrli, A. P. Marchand, S. Wherli, *Interpretation of C-13 NMR Spectra*, 2nd ed., Wiley, Chichester, **1988**, pp. 74–75.

[25] D. Casarini, L. Lunazzi, A. Mazzanti, *J. Org. Chem.* **1998**, *63*, 9125; see also: A. E. Aliev, K. D. M. Harris, *Magn. Reson. Chem.* **1994**, *32*, 366.

Exceptionally Long (≥ 2.9 Å) C−C Bonds between [TCNE]− Ions: Two-Electron, Four-Center π*−π* C−C Bonding in π-[TCNE]2 2−**

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Dedicated to the memory of Linus Pauling on the occasion of the 100th anniversary of his birth

We present here an exceptionally long C−C bonding interaction that has spectroscopic (IR and UV/Vis), structural, and magnetic properties expected for a bond and that complies with Pauling's definition of a chemical bond.[1] Strong carbon–carbon bonding is the essence of organic chemistry. The length of a C−C single bond, that is, 1.54 Å found in the diamond allotrope of carbon, is among the essential information learned by all organic chemistry students. This is the length of a single bond between sp^3-hybridized carbon atoms and is the longest of all common C−C bonds, although elongated C−C bonds as long as 1.73 Å have been reported.[2] These bonds form whenever two carbon atoms possessing an unpaired electron are close to each other (e.g., as occurs for two ·CH$_3$ radicals, which form ethane). When the carbon atoms are radical anions (or radical cations), due to their strong coulombic repulsion, bonds do not form. Thus, many electron transfer salts involving radicals are stable, and as a consequence exhibit interesting electrical and optical properties. Herein, however, we show that C−C interactions having all the properties of a chemical bond are present between pairs of [TCNE]− ions in some TCNE-based electron transfer salts, and that this type of bonding is present for many other reduced strong electron acceptors, for example, cyanil,[3] 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ),[4] perfluoro-7,7,8,8-tetracyano-*p*-quinodimethane (TCNQF$_4$),[5] and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).[6]

Strong organic electron acceptors (**A**) such as TCNE and TCNQ form stable electron transfer salts that contain [**A**]·−. These salts were crucial for the discovery and development of molecule-based metals,[7] which subsequently led to the discovery of molecule-based superconductors,[8] as well as molecule-based magnets.[9]

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