Structural Studies of Arylazo(α, α-dimethylbenzyl)malononitriles. Evidence against the Correlation between Bond Length and Reactivity in Bond Cleavage Reactions

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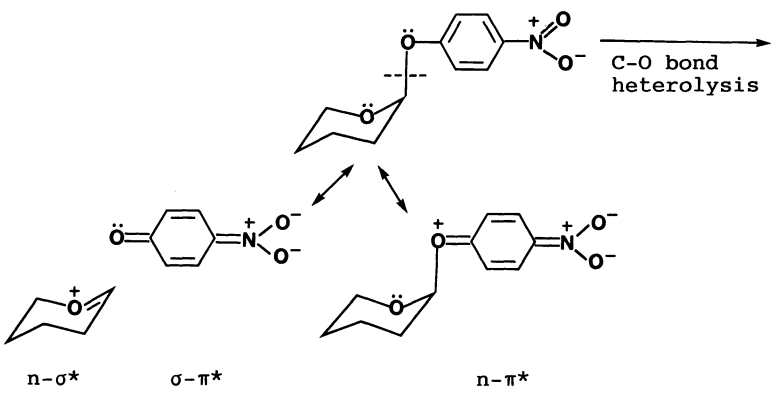
The X-ray structures of phenylazo(α, α-dimethylbenzyl)malononitrile and its *p*-MeO and *p*-NO_2 derivatives were determined to examine the relationship between reactivity and ground state geometry. Although the rate of C–C bond heterolysis increases in the order *p*-MeO < H ≪ *p*-NO_2, neither systematic elongation of the C–C bond nor indication of other geometrical changes due to the interaction between the σ orbital of the bond and the π system of an arylazo group was observed on going from *p*-MeO to *p*-NO_2. The results provide evidence against Kirby's proposal of a direct relationship between reactivity and bond length, and support Arnett's view that the stability of heterolysis products is not reflected in the bond length.

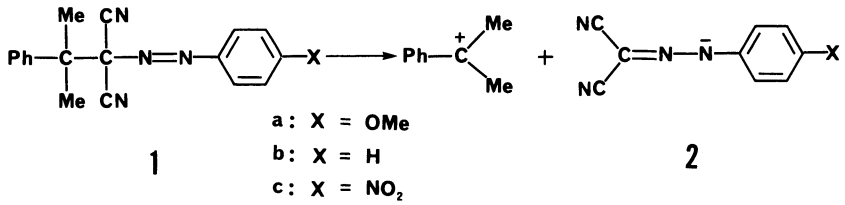
The long-standing argument in thermal unimolecular reactions involving bond cleavage is the problem of whether there exists a direct relationship between reactivity and ground state geometry such as bond length. Kirby and his co-workers have proposed two empirical rules:[1] (1) "The longer the bond, in a given system, the faster it breaks." (2) "The more reactive the system, the more sensitive is the length of the bond to structural variation." They claim that these rules hold commonly in any mode of bond cleavage. However, a serious problem arises from the fact that these rules are based on C–O bond heterolysis in 2-phenoxytetrahydropyrans and their analogues where an n–π* interaction between lone-pair electrons of the oxygen atom and the π system of the aryl moiety operates in the ground state (Scheme 1). Such an interaction may induce polarization of the C–O bond to be cleaved resulting in geometrical changes such as bond elongation as much systematically as the change in the heterolysis rate depending upon the nature of substituents. In this case, it should be pointed out that among substituent-induced geometrical variations only the changes arising from the σ–π* interaction between σ electrons of the C–O bond and a π system of the substituent can be correlated directly with the stability of the anions produced as illustrated below. It is however impossible to determine which interaction is the major contribution to geometrical variations.

What is the most important in gaining general acceptance is to examine whether the σ orbital of the bond in question involves a substantial component of the interaction with the orbital of substituents attached to the bond. The cleavage of a quaternary C–C bond is considered to be best suited for studies of this subject, since no n–π* type interaction is involved in the bond. A number of investigators who were interested in estimating reactivities of C–C bond cleavage from ground state geometries have so far been suspicious of a direct correlation of reaction rates with geometrical variations of the ground state in either homolytic[2–4] or heterolytic[5] bond cleavage as will be discussed later.

We reported that azo compounds **1a**—**c** undergo C–C bond heterolysis to generate the α-cumyl cation (α, α-dimethylbenzyl cation) and the leaving group anions **2** in polar solvents (Scheme 2) and that the heterolysis rate increases in the order *p*-MeO (**1a**) < H (**1b**) ≪ *p*-NO_2 (**1c**).[6] Recently, we have also reported the X-ray



Scheme 1.



Scheme 2.

Table 1. Crystal Data

Compound	**1a** (*p*-MeO)	**1b** (H)	**1c** (*p*-NO_2)
Mol formula	$C_{19}H_{18}N_4O$	$C_{18}H_{16}N_4$	$C_{18}H_{15}N_5O_2$
Mol wt	318.39	288.36	333.36
Crystal size/mm	0.3×0.3×0.2	0.8×0.2×0.2	0.6×0.1×0.2
D_c/g cm^{-3}	1.36	1.20	1.30
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	8.148(1)	9.873(2)	6.510(1)
b/Å	23.883(5)	9.460(2)	11.240(1)
c/Å	17.814(2)	10.432(4)	23.637(5)
α/deg	—	69.38(2)	—
β/deg	90.24(1)	111.73(2)	99.01(1)
γ/deg	—	115.39(1)	—
U/Å^3	3466.5(9)	795.6(4)	1708.4(4)
Z	8	2	4
$F(000)$	1344	304	696
μ/cm^{-1}	0.95	0.80	0.96
$2\theta_{max}$(deg) (λ=0.71069 Å)	55	55	55
No. of reflections used $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	4816	2131	1524
No. of collected independent reflections	8060	3600	3800
$R(=\Sigma\Delta/\Sigma\lvert F_o\rvert)$	0.054	0.049	0.043
R_w	0.065	0.052	0.038

W: **1a**, $1/[0.0043\lvert F_o\rvert^2 - 0.092\lvert F_o\rvert + 1.927]$; **1b**, $1/[6.68(\sin\theta/\lambda)^2 - 6.63(\sin\theta/\lambda) + 4.96]$; **1c**, $1/[0.0051\lvert F_o\rvert^2 - 0.0084\lvert F_o\rvert + 0.4985]$.

structure of the leaving group anion in the decomposition of **1c** (**2c** as the Et_4N^+ salt).[7] We have now determined the crystal structures of the three azo compounds **1a—c** to examine a correlation of the reactivity with the geometrical change in the ground state.

Experimental

X-Ray Structure Analyses. The cell dimensions and diffraction intensities were measured on a Rigaku Denki AFC-4 automatic four-circle diffractometer using graphite monochromated Mo $K\alpha$ radiation at room temperature. The structure was solved by MULTAN 78.[8] The hydrogen atoms were located in a difference Fourier map. The structural parameters were refined by a full-matrix least-squares method, using the UNICS III system.[9] Crystal data and the final R values are given in Table 1. Atomic coordinates for the three compounds **1a—c** are presented in Tables 2, 3, and 4, respectively. Full lists of hydrogen atom coordinates and other crystal data are deposited as Document No. 9028 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Rate Measurements. In order to calculate the activation parameters for decomposition of **1c** in MeCN-d_3, the rates were determined at three more temperatures as previously described.[6] 10^5k (s^{-1}): 40°C, 4.90; 50°C, 16.0; 60°C, 51.3 (Ref. 6); 70°C, 144. $\Delta H^{\ddagger}$=23.5±0.6 kcal mol^{-1}, $\Delta S^{\ddagger}$=−3.3± 1.7 eu. It follows that k=0.70×10^{-5} s^{-1} at 25°C.

Results and Discussion

Important bond lengths and bond angles are given in Tables 5 and 6 for the azo compounds **1a—c** and the hydrazonomalononitrile anion **2c**. The ORTEP drawings of these structures are shown in Fig. 1. The phenyl and arylazo groups in **1b** and **1c** are antiperiplanar to each other but they are synclinal in both of the two independent molecules in **1a**.

Changes in bond lengths and angles are rather small among these azo compounds. Furthermore, they are in almost perfect agreement with literature values in analogous compounds. The α-cumyl C(10)–C(13) bonds (1.523—1.539 Å) are longer by 0.02—0.04 Å than common sp^2–sp^3 C–C bonds, but are shorter than that in a crowded compound, 2,3-dimethyl-2,3-diphenylbutane (**3**) (1.545 Å).[10]

The central C–C bonds C(9)–C(10) [**1a**, 1.581(4); **1b**, 1.579(4); **1c**, 1.591(5) Å] which undergo heterolytic cleavage indicate that they are actually longer than normal sp^3–sp^3 C–C bonds and **1c** has the longest bond.

Table 2. Atomic Parameters ($\times 10^4$) and Their Equivalent Isotropic Temperature Factors for the Azo Compound **1a** (*p*-MeO)

Atom	Molecule A				Molecule B			
	x	*y*	*z*	B_{eq}/Å	*x*	*y*	*z*	B_{eq}/Å
C1	3560(3)	1048(1)	1350(1)	3.1(1)	8546(3)	1115(1)	4426(1)	3.2(1)
C2	4334(3)	573(1)	1624(2)	3.7(1)	9376(3)	652(1)	4161(2)	3.8(1)
C3	4425(3)	472(1)	2386(2)	3.9(1)	9478(3)	541(1)	3401(1)	3.6(1)
C4	3727(3)	850(1)	2880(1)	3.7(1)	8717(3)	898(1)	2899(1)	3.5(1)
C5	2940(3)	1329(1)	2606(2)	4.0(1)	7850(4)	1361(1)	3168(2)	4.2(1)
C6	2860(3)	1429(1)	1850(1)	3.6(1)	7771(3)	1474(1)	3919(1)	3.7(1)
C7	3305(3)	1059(1)	−896(1)	3.5(1)	8319(3)	1132(1)	6664(1)	3.3(1)
C8	4423(4)	1973(1)	−687(1)	4.1(1)	9509(3)	2041(1)	6461(1)	3.7(1)
C9	3018(3)	1604(1)	−516(1)	3.3(1)	8069(3)	1683(1)	6287(1)	3.0(1)
C10	1359(3)	1877(1)	−800(1)	3.6(1)	6441(3)	1967(1)	6577(1)	3.3(1)
C11	1493(5)	1981(2)	−1650(2)	5.0(1)	6600(4)	2059(2)	7427(2)	4.6(1)
C12	1173(5)	2452(1)	−421(2)	5.1(1)	6277(4)	2545(1)	6200(2)	4.6(1)
C13	−39(3)	1481(1)	−602(1)	3.6(1)	5007(3)	1581(1)	6373(1)	3.4(1)
C14	−664(4)	1101(1)	−1125(2)	4.9(1)	4332(3)	1216(1)	6892(2)	4.1(1)
C15	−1932(4)	744(2)	−943(2)	6.0(2)	3027(4)	872(1)	6704(2)	4.9(1)
C16	−2612(4)	756(2)	−236(2)	5.9(2)	2374(4)	884(1)	5990(2)	4.9(1)
C17	−2021(4)	1127(2)	287(2)	5.4(2)	3038(4)	1235(1)	5464(2)	4.9(1)
C18	−750(3)	1487(1)	107(2)	4.5(1)	4328(3)	1585(1)	5651(2)	4.0(1)
C19	4517(6)	316(2)	3956(2)	5.9(2)	9562(5)	355(2)	1844(2)	4.9(1)
N1	3546(2)	1106(1)	555(1)	3.3(1)	8543(2)	1182(1)	5218(1)	3.4(1)
N2	2996(2)	1556(1)	324(1)	3.3(1)	8026(2)	1635(1)	5446(1)	3.2(1)
N3	3504(3)	655(1)	−1215(1)	5.0(1)	8466(3)	721(1)	6966(1)	4.6(1)
N4	5475(4)	2274(1)	−807(1)	5.9(1)	10585(3)	2328(1)	6584(1)	5.3(1)
O1	3726(3)	796(1)	3639(1)	5.0(1)	8729(3)	834(1)	2145(1)	4.7(1)

Table 3. Atomic Parameters ($\times 10^4$) and Their Equivalent Isotropic Temperature Factors for the Azo Compound **1b** (H)

Atom	*x*	*y*	*z*	B_{eq}/Å	Atom	*x*	*y*	*z*	B_{eq}/Å
C1	8785(3)	4099(3)	8383(2)	3.5(1)	C12	9827(4)	2621(4)	5407(3)	5.0(2)
C2	7692(3)	2730(3)	8937(3)	4.8(1)	C13	12102(3)	1600(3)	6468(3)	4.0(1)
C3	6568(4)	2885(4)	9305(4)	5.5(2)	C14	12554(4)	257(4)	7170(3)	5.2(2)
C4	6520(3)	4398(4)	9098(3)	5.1(2)	C15	13754(5)	114(5)	6880(4)	6.6(2)
C5	7584(4)	5740(4)	8522(3)	4.9(2)	C16	14513(4)	1305(6)	5910(5)	7.0(2)
C6	8729(3)	5608(3)	8165(3)	4.3(1)	C17	14089(4)	2635(5)	5223(4)	6.4(2)
C7	12461(3)	4464(3)	7378(3)	3.8(1)	C18	12901(4)	2788(4)	5499(3)	5.0(2)
C8	12407(3)	2056(3)	9221(3)	3.6(1)	N1	10025(2)	4093(2)	7997(2)	3.6(1)
C9	11461(3)	2802(3)	7902(3)	3.5(1)	N2	10169(2)	2774(2)	8347(2)	3.8(1)
C10	10764(3)	1769(3)	6757(3)	3.8(1)	N3	13223(3)	5732(3)	6989(3)	5.5(1)
C11	9624(4)	120(3)	7326(4)	5.1(2)	N4	13094(3)	1471(3)	10251(3)	5.0(1)

Table 4. Atomic Parameters ($\times 10^4$) and Their Equivalent Isotropic Temperature Factors for the Azo Compound **1c** (*p*-NO_2)

Atom	*x*	*y*	*z*	B_{eq}/Å	Atom	*x*	*y*	*z*	B_{eq}/Å
C1	8780(5)	2191(3)	5059(1)	4.2(1)	C14	2535(6)	4637(4)	2760(2)	4.9(1)
C2	10328(6)	3051(3)	5116(2)	4.8(1)	C15	796(7)	4733(5)	2345(2)	6.0(1)
C3	12135(6)	2856(4)	5490(2)	4.9(1)	C16	−42(7)	3750(5)	2059(2)	6.5(2)
C4	12361(5)	1803(3)	5797(1)	4.5(1)	C17	892(7)	2667(5)	2177(2)	6.4(1)
C5	10848(6)	942(3)	5740(2)	5.0(1)	C18	2640(6)	2564(4)	2585(2)	5.3(1)
C6	9029(6)	1147(3)	5367(2)	4.8(1)	N1	6863(4)	2291(3)	4665(1)	4.6(1)
C7	3651(5)	4337(4)	4118(2)	4.8(1)	N2	6707(4)	3213(3)	4386(1)	4.8(1)
C8	3389(5)	2236(3)	3961(1)	4.4(1)	N3	2812(6)	5133(3)	4261(2)	7.4(1)
C9	4766(5)	3285(3)	3951(1)	4.1(1)	N4	2275(5)	1461(3)	3969(1)	6.3(1)
C10	5465(5)	3441(3)	3339(1)	4.1(1)	N5	14285(5)	1607(3)	6204(1)	5.9(1)
C11	6789(7)	2364(4)	3238(2)	5.6(1)	O1	15452(5)	2451(3)	6324(2)	9.1(1)
C12	6814(7)	4564(4)	3351(2)	5.4(1)	O2	14605(4)	635(3)	6418(2)	8.4(1)
C13	3512(5)	3549(3)	2888(1)	4.0(1)					

Table 5. Selected Bond Lengths (Å) for the Azo Compounds **1a**—**c** and the Hydrazono Anion **2c**

	1a (*p*-MeO)		**1b** (H)	**1c** (*p*-NO_2)	**2c**[7]
	A	B			
C(9)–C(10)	1.582(4)	1.579(3)	1.579(4)	1.591(5)	—
C(7)–C(9)	1.486(4)	1.489(4)	1.488(3)	1.474(5)	1.420(7)
C(8)–C(9)	1.478(4)	1.484(4)	1.483(3)	1.483(5)	1.417(7)
C(7)–N(3)	1.132(4)	1.126(4)	1.133(3)	1.127(5)	1.134(7)
C(8)–N(4)	1.139(4)	1.134(4)	1.134(3)	1.136(5)	1.138(7)
C(9)–N(2)	1.501(3)	1.503(3)	1.498(4)	1.501(4)	1.361(7)
N(1)–N(2)	1.233(3)	1.232(3)	1.228(3)	1.225(4)	1.257(6)
N(1)–C(1)	1.422(3)	1.420(3)	1.426(4)	1.439(4)	1.453(7)
C(10)–C(11)	1.537(4)	1.535(4)	1.548(3)	1.528(6)	—
C(10)–C(12)	1.539(4)	1.540(4)	1.540(4)	1.535(6)	—
C(10)–C(13)	1.523(4)	1.531(3)	1.539(5)	1.531(4)	—

Table 6. Selected Bond Angles (°) for the Azo Compounds **1a**—**c** and the Hydrazono Anion **2c**

	1a (*p*-MeO)		**1b** (H)	**1c** (*p*-NO_2)	**2c**[7]
	A	B			
C(11)–C(10)–C(13)	112.6(2)	112.4(2)	112.1(3)	112.4(3)	—
C(12)–C(10)–C(13)	112.2(2)	111.7(2)	111.5(3)	111.0(3)	—
C(11)–C(10)–C(12)	107.2(3)	108.0(2)	107.8(2)	108.6(3)	—
N(1)–N(2)–C(9)	113.2(2)	112.8(2)	113.1(2)	113.9(3)	112.4(4)
N(2)–C(9)–C(7)	112.8(2)	112.7(2)	112.4(2)	104.9(3)	115.1(4)
N(2)–C(9)–C(8)	105.4(2)	105.5(2)	104.3(2)	113.1(3)	126.4(4)
N(2)–C(9)–C(10)	109.7(2)	110.0(2)	109.5(2)	107.4(2)	—
C(7)–C(9)–C(8)	107.7(2)	108.0(2)	108.3(2)	108.0(3)	118.5(4)

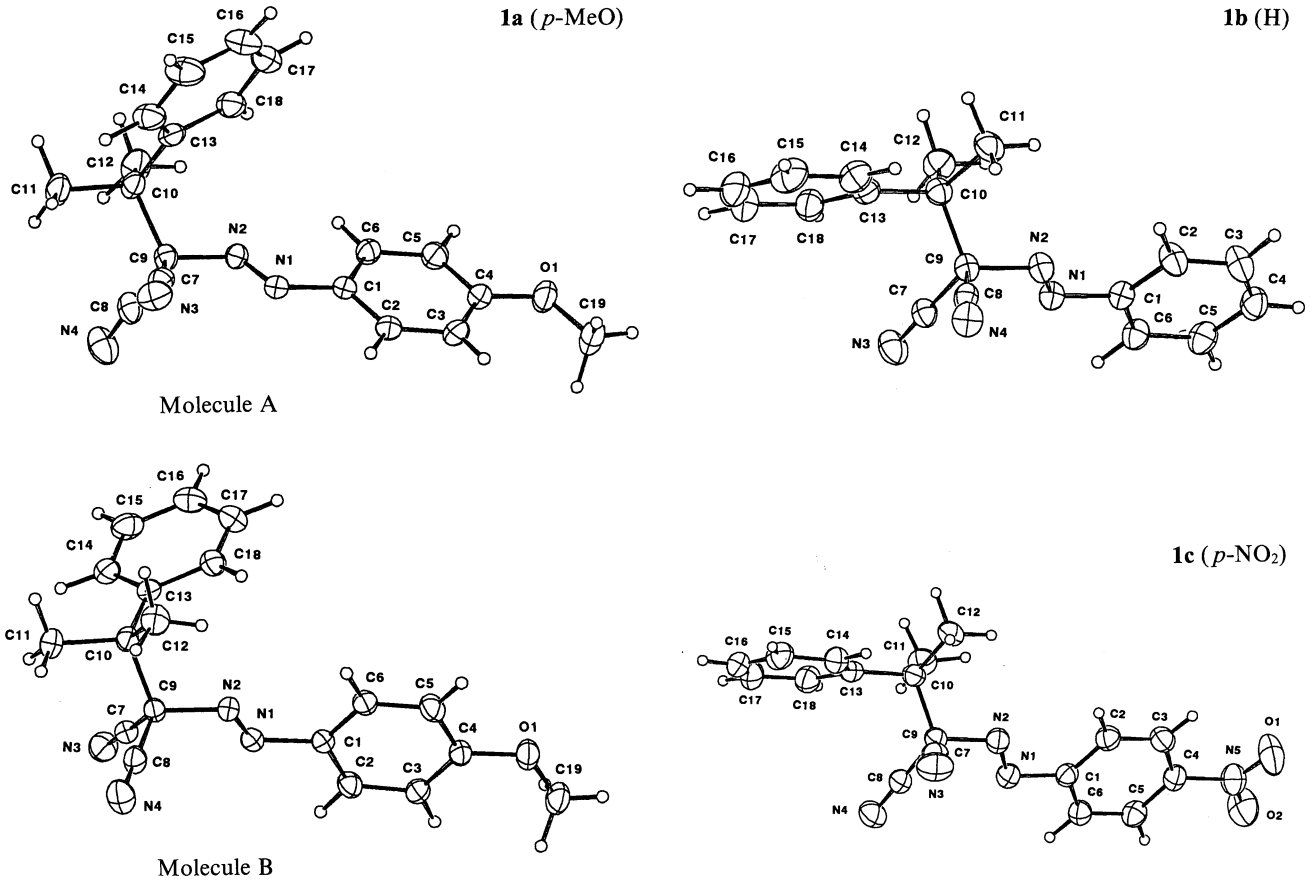
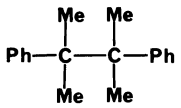


Fig. 1. ORTEP drawings of the azo compounds **1a**—**c**.

However, the substituent effect on bond length is small contrary to the large effect on the reactivity of heterolysis [$k\times10^5$ (s^{-1}) in methanol-d_4 at 60°C: **1a**, 0.18; **1b**, 0.82; **1c**, 97.2, and thus **1a**(*p*-MeO) : **1b**(H) : **1c**(*p*-NO_2)= 0.2 : 1 : 120].

The steric congestion around the bond is one of the factors affecting the bond length and the molecular mechanics calculation (MM2) may be a useful tool to evaluate the extent of the steric effect. With a crowded ethane **3**, it has been reported that the calculated central C–C bond length (1.574 Å) is close to the observed value (1.585 Å).[10]



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Molecular mechanics calculations were performed using the MM2(82) program[11] with incorporation of several parameters for the azo linkage.[12] The calculation for the azo compound **1** exhibits no difference in the bond length of the present concern between antiperiplanar and synclinal conformation. The calculated bond length (1.558 Å) is shorter by 0.02—0.03 Å than the observed C(9)–C(10) bond lengths for **1**, suggesting that the bond elongation may not be attributed only to the steric effect. We consider that a part of the bond elongation in the azo compounds **1** results from bond polarization due to the inductive effect of the three electronegative qroups attached to the C(9) atom, which would make the bond for the *p*-nitro derivative **1c** the longest.

There is no sign of contribution of the σ–π^* type interaction to the bond elongation. If some part of bond elongation results from the σ–π^* type interaction, the geometry of the arylazodicyanomethyl moiety should resemble that of the hydrazonomalononitrile anion more closely in the *p*-nitro derivative than in the others. As previously described,[7] the hydrazonomalononitrile anion **2c** has a planar structure (Fig. 2) and a comparison of the structural data for the hydrazonomalononitrile anion with those for the undissociated hydrazone points to the presence of extensive charge delocalization responsible for the hydrogen bond-insusceptible behavior of the anion which has been observed both in the rate of heterolysis for **1c**[6] and in the enthalpy of solution for the salt.[13]

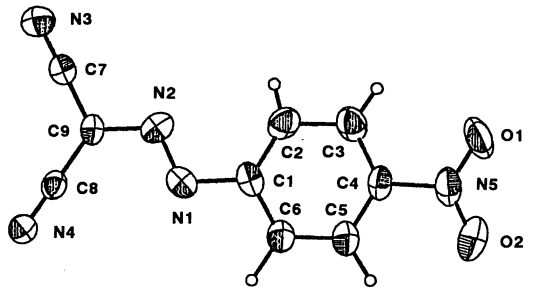


Fig. 2. ORTEP drawing of the conjugate base of *p*-nitrophenylhydrazonomalononitrile (hydrazonomalononitrile anion **2c**) as the tetraethylammonium salt.[7]

We carefully examined our structural data in which our attention was paid to geometrical changes in the arylazodicyanomethyl moiety, especially in the bond angles around the terminal carbon atom C(9) and in the lengths of the single bonds involving this carbon, i.e., C(9)–N(2), C(7)–C(9), and C(8)–C(9), as well as in the lengths in the azo and cyano groups. The bond angles around C(9) indicate that this atom is of typical sp^3 hybridization in all azo compounds examined. The bond lengths are compared in Fig. 3. The bonds C(7)–C(9) and C(8)–C(9) are shorter by 0.06 Å and the bond N(1)–N(2) is longer by 0.03 Å in the hydrazonomalononitrile anion **2c** than in the azo compounds **1**. The variation in bond length with reactivity is however not systematic and there is no evidence for the higher geometrical resemblance to the hydrazonomalononitrile anion in the *p*-nitro azo compound **1c** than in the *p*-methoxy and unsubstituted azo compounds (**1a** and **1b**). The crucial decision has been made by the fact that shortening of the C(9)–N(2) distance due to a charge-

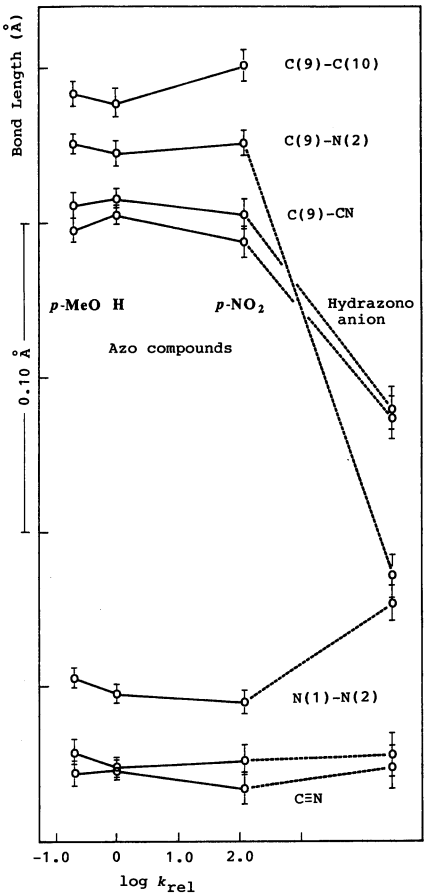


Fig. 3. Plot of bond lengths against the reactivity of heterolysis (the geometry of the *p*-MeO derivative was taken from molecule A).

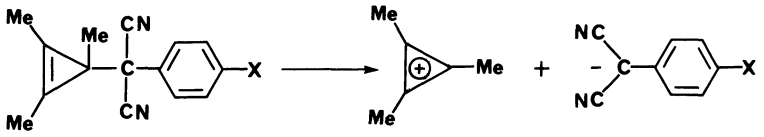
transfer interaction from the C–C bond to the *p*-nitrophenylazo moiety is not observed: A large difference in the length of this bond between the hydrazonomalononitrile anion **2c** and **1a** (0.14 Å) entirely holds between **2c** and **1c**.

Arnett and his co-workers reported the reversible C–C bond heterolysis of aryl(trimethylcyclopropenyl)malononitriles (**4**) (Scheme 3).[5] They found that the bond in question is significantly long in the *p*-nitro derivative **4c** [1.588(4) Å] but claimed that the stability of the heterolysis product is not reflected in the bond length because the *p*-methoxy derivative **4a** is less dissociative but it still has a long bond [1.581(3) Å] [k(s^{-1}) in MeCN-d_3 at 25 °C: **4c**, 5.6×10^{2}; **4a**, 8.6×10^{-1} (the latter value was estimated from the Hammett equation with R=0.989)[5]].

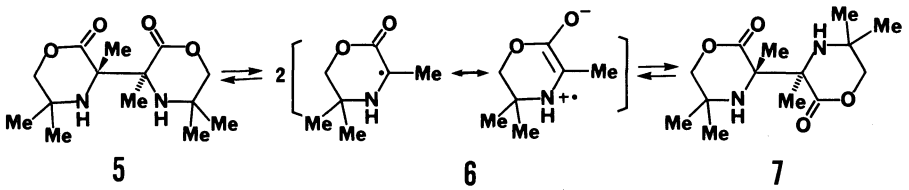
In each of the heterolysis systems **1** and **4**, the change in reactivity on the *p*-substituent from OMe to NO_2 is within the order of 6.5×10^{2} in the relative rate ($\Delta\Delta G^{\neq}$, −4 kcal mol^{-1}). Both systems are of the heterolysis of quaternary C–C bonds. We therefore consider that the two systems are worth being compared as the reactions of the same mode of cleavage, as previously discussed briefly.[14] Compound **4c** dissociates much faster than the azo compound **1c** (k_{rel}=8.1×10^{7} in MeCN-d_3 at 25 °C; $\Delta\Delta G^{\neq}$, −11 kcal mol^{-1}). Such an enormous difference in reactivity comes from the extremely high stability of the cyclopropenium ion produced from compound **4**. On the other hand, the length of the C–C bond to be cleaved in **4c** is almost the same as that in **1c**. The result strongly suggests that the length of C–C bonds in the ground state is insensitive to the stability of carbocations produced via the heterolysis of the bonds, even though it should be taken into consideration that the bond in **1c** involves a cyclopropenyl carbon. The fact that there is no systematic change in bond length in our reaction system as well as in a much more reactive system of the Arnett group are inconsistent with both of the rules proposed by the Kirby group. Consequently, in support of the Arnett's view, we can state with certainty that C–C bond lengths are not related to the magnitude of charge dispersal in the transition state for heterolysis; in other words, there is no significant mixing of the σ orbitals of the elongated covalent C–C bonds with the π orbitals of the groups attached to each carbon atom in the ground state.

To the best of our knowledge, the discussion on the present subject started from the studies of C–C bond homolysis. Bioxazinones **5** and **7** reported by Koch and his co-workers[2] have an unusually weak C–C bond and readily interconvert via a radical **6** (Scheme 4). Captodative stabilization of the radical **6** has been suggested, since the enthalpy of activation for the homolysis **5**→**6** is solvent dependent and is extremely reduced in protic solvents [$\Delta H^{\neq}$(kcal mol^{-1}), $\Delta S^{\neq}$ (eu): 27.3, 6.7 in $CHCl_3$; 22.6, 6.6 in methanol]. Elongation of the central C–C bond in *dl* dimer **5** [1.598(5) and 1.583(5) Å for the two independent molecules in the asymmetric unit, respectively] has been attributed primarily to steric strain. Our MM2 calculation well reproduced the X-ray geometries with a slightly shorter central C–C bond (1.578 Å). It is therefore likely that bond elongation is essentially attributable to the steric effect. The possibility of electronic through-bond coupling of the amino and carboxyl moieties, which should be related to the radical stability, has been ruled out, not only because all the bonds next to the central C–C bond are of approximately normal length, but because compounds **5** and **7** show no ultraviolet absorption due to through-bond coupling.

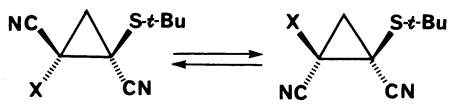
The homolytic system reported by Viehe and his co-workers is in a similar situation (Scheme 5).[3] The cyclopropane **8** has only one captodative center and requires a 5 kcal mol^{-1} higher activation energy for the trans–cis isomerization than the cyclopropanes **9** and **10** in which two carbons in the cyclopropane ring are captodatively substituted: E_a(t→c) **8**, 31.7; **9**, 26.9; **10**,



Scheme 3.



Scheme 4.



8: X = CO_2Me
9: X = SPh
10: X = Ph

Scheme 5.

26.7 kcal mol^{-1}. However, the longest C–C bond has been found in the cyclopropane showing the highest energy barrier: **8**, 1.580(4); **9**, 1.557(5); **10**, 1.555(5) Å. It has therefore been suggested that the facile isomerization is not a consequence of a destabilized ground state but of an increased spin delocalization in the transition state. Interestingly, the order of bond length for the cyclopropanes (**9,10**<**8**) resembles that for the azo compounds (**1a,1b**<**1c**) as well as that for the cyclopropenes (**4a**<**4c**) in that the compound having the longest bond involves a carbon substituted by the most strongly electron-withdrawing group in a system.

Homolysis reactions generating simple radicals without spin or charge delocalization such as the bond cleavage of hexaalkylethanes reported by Rüchardt and his co-workers exhibit a good correlation between reactivity and bond length, since the major factor diminishing the energy barrier to homolytic cleavage is relief of the steric congestion causing bond elongation in the ground state.[15] However, they have found a contradictory case in which the C–C bond suffering homolytic cleavage is not the longest one in the molecule. In view of this finding together with a large stock of their experimental data, they put forward that the length of a bond is no criterion for its strength.[4]

Conclusions

The reactivity of thermal unimolecular bond cleavage is affected by steric and electronic effects. As far as the steric effect is concerned, a direct relationship between reactivity and bond length would be expected, since the steric congestion that causes bond elongation in the ground state is relieved in the transition state. However, if substituents possess π or n orbitals, spin or charge delocalization during bond cleavage becomes the major factor affecting bond lability. The present argument concerns whether there exists the contribution of this type of delocalization to ground state geometries, and is a matter of the energy difference between σ orbitals (σ or σ*) of the bond and the π or n system of substituents being perturbed.

Our data and other investigators' cited above indicate that energy differences between the orbitals relevant to σ–π* and π–σ* interactions are large enough to be able to ignore perturbation in common C–C single bonds, which therefore work as good insulators against the electron demand or supply from substituents. The mixing of the σ orbitals with π systems would take place only in a molecule activated toward the transition state under suitable reaction conditions, but not in crystals at ambient temperature. Exceptional are cases of highly strained compounds such as semibullvalenes, in which both π–σ* and σ–π* interactions in the ground state may serve as the factors determining the barrier to bond cleavage, because only a small energy difference is expected between σ and π orbitals. However, generally speaking, an efficient interaction between σ and π orbitals seems unlikely as compared with n–σ* type interactions with a smaller energy difference between the orbitals, and thus caution may be needed to prevent the erroneous assignment of experimental results to σ–π* and π–σ* interactions in the ground state.

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