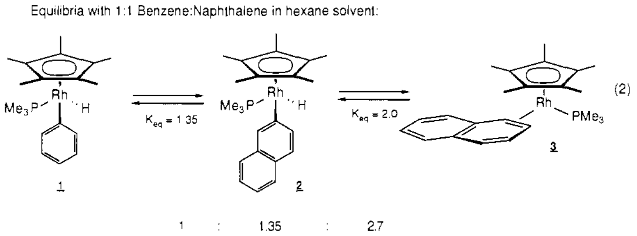
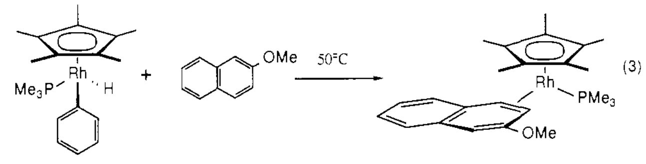
none of these cases is any evidence for competitive C–H bond activation seen. Taube has also recently reported many examples[13] of η^2-arene coordination to $[Ru(NH_3)_5]^{2+}$ and $[Os(NH_3)_5]^{2+}$, and Graham has found evidence for η^2-coordination of arene upon protonation of CpRe(NO)(CO)(Ph).[14]

Other fused, polycyclic aromatics also react under conditions of thermal equilibrium to give η^2-arene complexes. Upon heating a 10:10:1 solution of benzene/naphthalene/**1** in hexane for 24 h, three species are observed. The ^{31}P NMR spectrum in C_6D_{12} shows three doublets (δ 7.90, J = 156 Hz; δ 7.63, J = 155 Hz; δ 0.66, J = 203 Hz) in a 1:1.35:2.7 ratio, consistent with the formation of two Rh(III) complexes and one Rh(I) complex (eq 2). One of the Rh(III) complexes can be identified as **1** by comparison with an authentic sample. The second Rh(III) complex is identified as $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})H$ (**2**) on the basis of 400-MHz ^1H COSY NMR data and independent preparation. The third product is formulated as $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-naphthalene})$ (**3**), also on the basis of ^1H NMR data.[15] The ^1H NMR spectrum shows a pair of coupled multiplets at δ 3.629 and 3.213 for the hydrogens on the double bond bound to rhodium. The higher field resonance also couples to one of the aromatic hydrogens at δ 6.570. The η^2-naphthalene/naphthyl hydride isomers can also be formed by direct synthesis. A 1:2 mixture of complexes **2** and **3** is also formed upon reduction of $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Br$[16] with Na[HB($s$-Bu)$_3$].



The above observations indicate that under equilibrium conditions *the η^2-naphthalene complex **3** is thermodynamically preferred over the C–H oxidative addition adduct **2**, and that both of these are more stable than the phenyl hydride **1**.* This system is the first example in which reversible arene activation and η^2-coordination are both observed. It is interesting to note that in 1965 Chatt described the chemical behavior of $Ru(dmpe)_2(naphthyl)H$ as if the compound were a complex of naphthalene.[17]

We are not certain of the factors that lead to the stabilization of the η^2-naphthalene adducts. Introduction of a 2-methoxy substituent leads to only one product under similar thermal equilibrium conditions, the (3,4-η^2)-methoxynaphthalene complex (eq 3).[18] The electron-donating methoxy group apparently stabilizes even further the η^2-naphthalene complex. We believe that the added stability of these adducts might be associated with the resonance energy that remains following η^2-coordination. With naphthalenes, the fused aromatic system leaves behind a styrene residue, whereas with phenanthrene, a biphenyl moiety remains. Comparison of the heat of hydrogenation of benzene to cyclohexadiene to that for hydrogenation of naphthalene to 1,2-dihydronaphthalene indicates an ~8 kcal/mol preference for the latter reaction.[19] Earlier reports of simple Hückel calculations on the effects of η^2 binding of an arene to a metal support the notion that binding of fused aromatic complexes costs less in terms of resonance energy.[8b] Future studies will continue to investigate the factors that control this equilibrium.



Acknowledgment is made to the U.S. Department of Energy (DE-FG02-86ER13569) for their partial support of this work. W.D.J. also thanks the Camille and Henry Dreyfus Foundations for awards.

Registry No. 1, 81971-46-2; **2**, 123099-42-3; **3**, 123099-43-4; $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-phenanthrene})$, 123099-41-2; $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})Br$, 123099-44-5; Na[HB($s$-Bu)$_3$], 67276-04-4; $(C_5Me_5)Rh(PMe_3)((3,4\text{-}\eta^2)\text{-2-methoxynaphthalene})$, 123099-45-6.

Supplementary Material Available: Tables listing atomic coordinates, anisotropic thermal parameters, and bond distances and angles for $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-phenanthrene})$ (10 pages); calculated and observed structure factors for $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-phenanthrene})$ (17 pages). Ordering information is given on any current masthead page.

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[13] Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883–1885. Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 2917–2918. Cordone, R.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 8101–8102. Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439–2445. Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5403–5407. Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725–5731. Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7555–7556. Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7906–7907.

[14] Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305–306. Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135–140.

[15] For $(C_5Me_5)Rh(PMe_3)(2\text{-naphthyl})H$ ^1H NMR (c-C_6D_{12}): δ 1.080 (d, J = 8.0 Hz, 9 H), 1.814 (d, J = 1.2 Hz, 15 H), 7.047 (t, J = 8.2 Hz, 1 H), 7.127 (t, J = 7.5 Hz, 1 H), 7.188 (d, J = 8.2 Hz, 1 H), 7.407 (d, J = 8.1 Hz, 1 H), 7.456 (d, J = 8.2 Hz, 1 H), 7.493 (d, J = 8.1 Hz, 1 H), 7.694 (s, 1 H), −13.549 (dd, J = 49.8, 32.3 Hz, 1 H). For $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-naphthalene})$ ^1H NMR (c-C_6D_{12}): δ 1.180 (d, J = 8.0 Hz, 9 H), 1.301 (d, J = 2.6 Hz, 15 H), 3.213 (td, J = 7.4, 2.5 Hz, 1 H), 3.629 (td, J = 7.4, 2.5 Hz, 1 H), 6.564 (d, J = 0.5 Hz, 1 H), 6.570 (dd, J = 4.5, 0.5 Hz, 1 H), 6.889 (t, J = 7.5 Hz, 1 H), 7.041 (t, J = 7.5 Hz, 1 H), 7.109 (d, J = 7.7 Hz, 1 H), 7.275 (d, J = 7.7 Hz, 1 H).

[16] Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376–2388.

[17] Chatt, J.; Davidson, M. M. *J. Chem. Soc.* **1965**, 843–855.

[18] For $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-2-methoxynaphthalene})$ ^1H NMR (c-C_6D_{12}): δ 1.187 (d, J = 8.1 Hz, 9 H), 1.310 (d, J = 2.6 Hz, 15 H), 3.043 (dt, J = 7.3, 2.4 Hz, 1 H), 3.678 (dt, J = 7.8, 2.6 Hz, 1 H), 3.721 (s, 3 H), 5.750 (s, 1 H), 6.848 (t, J = 7.4 Hz, 1 H), 6.912 (t, J = 7.4 Hz, 1 H), 7.029 (d, J = 7.2 Hz, 1 H), 7.218 (d, J = 7.5 Hz, 1 H). ^{31}P NMR (C_6D_{12}): δ 0.39 (d, J = 201 Hz).

[19] Based on heat of formation data for C_6H_6(l), C_6H_8(l), $C_{10}H_8$(s), and $C_{10}H_{10}$(l) from: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data for Organic Compounds*; Chapman and Hall: New York, 1986. Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons: New York, 1969.

Electronic Effects on the Addition of Double Bonds to Triplet Benzenes: What Is the Rate-Determining Step in Biradical Formation?

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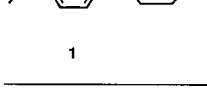
We recently reported that acetophenones containing o- or p-3-buten-1-oxy substituents undergo rapid internal triplet quenching that leads to 2 + 2 cycloadducts.[1,2] Whereas the reaction of alkenes with excited singlet benzenes has been widely studied,[3] the corresponding triplet reaction is basically unknown. Therefore we have measured rate constants and Arrhenius parameters for a variety of such unsaturated acetophenones in order to establish the nature of the interaction that quenches the excited triplet and leads to product.



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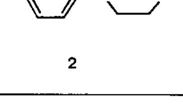

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[1] Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 4404.

[2] Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 6528.

[3] (a) Gilbert, A. *Pure Appl. Chem.* **1980**, *52*, 2669. (b) Mattay, J. *Tetrahedron* **1985**, *41*, 2405.

Table I. Arrhenius Parameters for Triplet Decay[a] of Alkenoxyacetophenones **1–3**

R	X	log *A*	E_a[b]	k_{300},[c] 10^8 s^{-1}
		Para (**1**)		
CH=CH$_2$	CN	10.6 ± 0.1	3.1 ± 0.1	2.2
CH=CH$_2$	Cl	10.8 ± 0.1	4.0 ± 0.1	0.9
CH=CH$_2$	H	10.5 ± 0.2	3.9 ± 0.2	0.45
CH=CH$_2$	H[d]	10.5 ± 0.17	3.9 ± 0.16	0.45
CH=CH$_2$	CH$_3$	10.5 ± 0.06	4.3 ± 0.06	0.20
CH=CH$_2$	OCH$_3$	10.7 ± 0.2	5.0 ± 0.2	0.12
CMe=CH$_2$	H	10.9 ± 0.1	4.6 ± 0.1	0.38
CMe=CH$_2$	F	11.3 ± 0.2	5.0 ± 0.2	0.40
CH=CMe$_2$	CH$_3$	11.1 ± 0.2	3.6 ± 0.2	2.7
CH$_2$CH=CH$_2$	H			≤0.01[e]
		Meta (**2**)		
CH=CH$_2$				≤0.02[e]
CH=CMe$_2$				≤0.03[e]
		Ortho (**3**)		
CH=CH$_2$		10.2 ± 0.27	3.5 ± 0.29	0.37

[a] In toluene unless noted. [b] Kilocalories per mole. [c] Extrapolated. [d] In methanol. [e] Actual measurement.

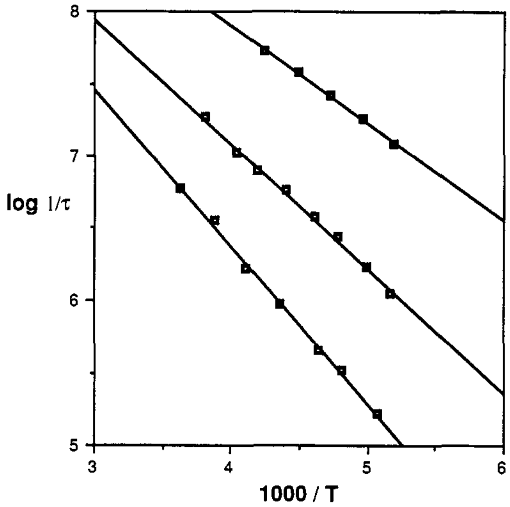


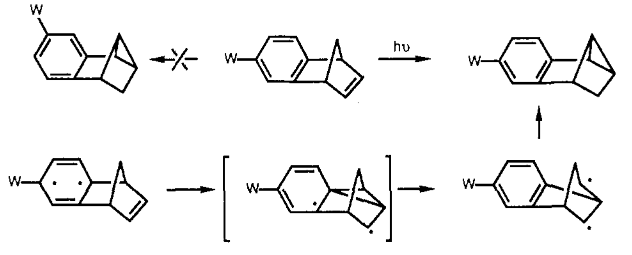
Figure 1. Temperature dependence of triplet lifetimes of three *p*-butenoxyacetophenones **1**: top, X = CN; middle, X = H; bottom, X = OCH$_3$.

Table I lists the various compounds that have been studied. They were synthesized by S$_N$2 displacements on 4-bromobutenes by acylphenolates, most of which were synthesized by Fries rearrangements of the appropriately substituted phenyl acetates. The kinetic measurements were performed with 337-nm (nitrogen laser) excitation of deaerated solutions approximately 3 × 10^{-3} M in ketone. Decay of the strong triplet ketone transient absorbance was monitored at several wavelengths between 370 and 420 nm.[4] The samples displayed clean exponential decays between 0 and −80 °C in toluene or methanol solvent. Figure 1 shows typical Arrhenius plots.

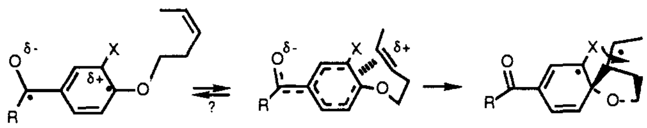
For R = vinyl, log *A* = 10.6 ± 0.1 for all of the *p*-butenoxy ketones, and the E_a values vary by only 2 kcal/mol. The ortho-substituted ketone seems to have slightly lower *A* and E_a values. Alkyl substitution on the double bond raises *A* values; it raises E_a when internal and lowers E_a when terminal. However, all of the changes are small.

There are five separate important rate comparisons. Two have already been reported:[1] the reaction is rapid (1) only when three atoms separate the double bond from the benzene ring (10th entry in Table I) and (2) only for phenyl alkyl ketones, not for benzophenones. The latter fact demonstrates the involvement specifically of π,π* triplets.[5] Both ortho- and para-substituted ketones react rapidly, whereas their meta isomers give only long-lived triplets that do not cycloadd. Alkyl substitution speeds up the reaction only when it is on the terminus of the double bond. Finally, electron-withdrawing substituents ortho to the unsaturated ether group enhance reactivity, while similar electron-donating substituents depress reactivity.

The positional selectivity of this reaction is shared by the di-π-methane rearrangement of benzonorbornadienes. In particular, Paquette has shown that cyano and acetyl substituents direct the rearrangement such that the double bond bridges to the benzene ring only ortho or para, never meta.[6] This selectivity is in accord with the fact that spin density in triplet benzonitriles (and by extension in the π,π* triplets of acetophenones) is high only para and ortho[7,8] and suggests a radical-like process.



We have already suggested that this new cycloaddition reaction involves first CT interaction between donor double bond and acceptor triplet benzene, followed by biradical formation.[1] The facile cis–trans isomerization of the double bond strongly implicates the intermediacy of a biradical. The ring-positional selectivity, the rapid formation only of five-atom rings, and the effects of alkyl substitution on the double bond[9] all would result if biradical formation were rate-determining, with cyclization of the 5-hexenyl radical as the model.[9]



How necessary is the postulated first CT process? Certainly the effect of a third ring substituent indicates that the triplet benzene acts as an electron acceptor at the transition state. The absolute maximum change in E_a is small, corresponding to a rate ratio of only 20 at room temperature. However, the 2 kcal/mol spread in E_a values is half of the 3.9 kcal/mol value for the unsubstituted case. In fact, the value is significantly lower than the 6.1 kcal/mol E_a measured for cyclization of 5-hexenyl radicals.[10] Given the known CT quenching of triplet phenyl ketones by alkenes,[11,12] we feel that the 70–71 kcal/mol triplet excitation energy of the alkoxyacetophenones can promote sufficient CT interaction to lower the activation energy for radical cyclization, such that both steps have barriers of similar energy. Thus a 3-methyl substituent on the 3-butenoxy group has almost no effect; it would enhance reactivity if CT dominated[11] and depress reactivity if radical addition dominated.[9] This is another example of a two-step bifunctional process in which both steps are partially rate-determining.[13]

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(4) For a discussion of the apparatus, see: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(5) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7335.

(6) Paquette, L. A.; Cottrell, D. M.; Snow, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 3723.

(7) Wagner, P. J.; May, M. J. *Chem. Phys. Lett.* **1976**, *39*, 350.

(8) Hirota, N.; Wong, T. C.; Harrigan, E. T.; Nishimoto, K. *Mol. Phys.* **1975**, *29*, 903.

(9) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 185–201.

(10) Schmid, P.; Griller, D.; Ingold, K. U. *Int. J. Chem. Kinet.* **1979**, *11*, 333.

(11) (a) Caldwell, R. A.; Sovocool, G. W.; Gajewski, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 2549. (b) Kochevar, I. E.; Wagner, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 3859.

(12) Morrison, H.; Trisdale, V.; Wagner, P. J.; Liu, K. C. *J. Am. Chem. Soc.* **1975**, *97*, 7189.

(13) Wagner, P. J.; Truman, R. H.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727.

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The Nature of Halogen···Halogen Interactions: Are Short Halogen Contacts Due to Specific Attractive Forces or Due to Close Packing of Nonspherical Atoms?[1a]

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The nature of halogen···halogen interactions in crystals has long been a matter of interest and debate.[2] Intermolecular interactions associated with distances shorter than the sum of the van der Waals radii of contacting atoms have been variously referred to earlier[3] as "donor–acceptor" interactions, "secondary" interactions, and "charge transfer" interactions and, more recently,[4-6] as interactions between the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals (HOMO–LUMO) or "incipient electrophilic and nucleophilic attack".[4,5] In all such interactions, it has been noticed[4,5] that there is a directional preference with which contacting groups position themselves relative to each other. For example, halogen···halogen contacts[4c,7] have two preferred geometries, type I ($\theta_1 = \theta_2$) or type II ($\theta_1 = 180°$, $\theta_2 = 90°$), where θ_1 and θ_2 are the two C–Cl···Cl angles. A delimma arises since these preferred geometries may result due to either (i) specific attractive forces in certain directions[4-5,8] (i.e., increased attraction) or (ii) nonspherical shapes with polar flattening[7,9] in a close-packed crystal (i.e., decreased repulsion). In the first case, it is implied that the short and directional halogen···halogen contacts are caused by the specific attractive forces, whereas in the second case, they are due to the close packing of nonspherical atomic moieties of molecules. Computationally, both alternatives have been modeled either with special bonding terms[8] or with anisotropic atom potentials for halogen atoms.[9] While these computational methods might permit a better fit of structure to observed properties of halogenated organic crystals, they do not provide real physical insight into the nature of these interactions. In this communication, we examine whether the halogen···halogen contacts are attractive or not.

Table I.[a] Intermolecular Contacts from Halogen Atoms to Halogen, Hydrogen, and Carbon Atoms in Halogenated Hydrocarbon Crystals

	contact type	distance, Å (less than)	no of contacts	correctn factor: *P*	corrected no. of contacts
fluorohydrocarbons (45)	F···F	2.94	25	0.19	132
	F···H	2.67	43	0.17	253
	F···C	3.22	46	0.64	72
chlorohydrocarbons (108)	Cl···Cl	3.52	147	0.27	544
	Cl···H	2.96	73	0.17	429
	Cl···C	3.51	74	0.56	132
bromohydrocarbons (58)	Br···Br	3.72	24	0.13	185
	Br···H	3.06	20	0.27	74
	Br···C	3.61	18	0.61	30
iodohydrocarbons (18)	I···I	3.96	12	0.31	39
	I···H	3.18	1	0.23	13
	I···C	3.73	7	0.46	15

[a] Van der Waals radii in Å: F, 1.47, Cl, 1.76, Br, 1.86, C, 1.75, H, 1.20.

There is evidence that indicates that the primary cause of directional halogen···halogen interactions is the specific attractive forces, and the nonspherical shapes or polar flattening is the resulting effect. The gas-phase molecular beam scattering experiments by Klemperer and co-workers[10] show that $(X_2)_2$ (X is a halogen) and F–Cl···F–H form complexes. Also, the "L" shape and the stereochemistry of the cluster and the complex not only follow the molecular orbital calculations[11] but also are in perfect agreement with the directional interactions seen in the solid state.[4c] Since close packing is not involved in deciding the gas-phase stereochemistry (which, incidentally, agrees with the solid-state stereochemistry), the dilemma is resolved in the gas phase and it is clear that the primary cause for the directional preferences of halogen···halogen interactions is the attractive forces.

To resolve the dilemma in the solid state, we have employed a statistical approach. In a close-packed crystal where no directional forces are invoked, it is reasonable to assume that the number of intermolecular contacts to any given atom is nearly proportional to the exposed surface area of that atom. If, in a group of compounds, halogen···halogen contacts are observed in numbers greatly out of proportion to the average ratio of halogen to total surface area, these interactions must be attractive in nature. Conversely, if these contacts are observed in numbers that approximately conform to the ratio of halogen to total area, the structures are close-packed and the observed intermolecular geometries must be due to the ellipsoidal shapes of the halogen moieties. *Though both the increased attraction and reduced repulsion give rise to the same geometry for C–X···X–C interactions, the number of such interactions in a given class of compounds will depend on the nature of the interaction.* So the key question is, Is the number of halogen···halogen contacts greatly out of proportion to the average ratio of halogen to total surface area or not?

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(1) (a) Work at Roswell Park supported in part by the National Institutes of Health, Grant CA 23704. Contribution no. 5146 from the Central Research and Development Department, E. I. du Pont de Nemours and Company. (b) Central Research and Development Department, E. I. du Pont de Nemours and Company. (c) Permanent address: School of Chemistry, University of Hyderabad, P.O. Central University, Hyderabad 500134, India. (d) Center for Crystallographic Research, Roswell Park Memorial Institute.

(2) Kitaigorodskii, A.; Pertsin, A. J. *The Atom-Atom Potential Method*; Springer: Berlin, 1987; pp 105–112. Yamasaki, K. *J. Phys. Soc. Jpn.* **1962**, *17*, 1262–1267. Nyburg, S. C. *J. Chem. Phys.* **1964**, *40*, 2493–2501. Nyburg, S. C. *J. Chem. Phys.* **1968**, *48*, 4890–4895. Hillier, I. H.; Rice, S. A. *J. Chem. Phys.* **1967**, *46*, 3881–3889. Wheeler, C. L.; Colson, S. D. *J. Chem. Phys.* **1976**, *65*, 1227–1235. Pertsin, A. J.; Ivanov, Y. P.; Kitaigorodskii, A. I. *Acta Crystallogr.* **1987**, *A37*, 908–913. Pertsin, A. J.; Ivanov, Y. P. *Chem. Phys. Lett.* **1985**, *116*, 176–179. Bonadeo, H.; D'Alessio, E. *Chem. Phys. Lett.* **1973**, *19*, 117–119. Burgos, E.; Murthy, C. S.; Righini, R. *Mol. Phys.* **1982**, *47*, 1391–1403. Mirsky, K.; Cohen, M. D. *Acta Crystallogr.* **1978**, *A34*, 346–348.

(3) (a) Bent, H. A. *Chem. Rev.* **1968**, *68*, 587–648. (b) Bent in his excellent review of donor–acceptor interactions has discussed the development of early ideas with examples and has pointed out the equivalence of several different ways of describing such intermolecular interactions; see especially pp 609–611. For previous work in this area, see also: Miller, R. S.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1974**, *96*, 6334–6339. Murray-Rust, P.; Motherwell, W. D. S. *J. Am. Chem. Soc.* **1979**, *101*, 4374–4376. Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222–228. Desiraju, G. R. In *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987; pp 519–546.

(4) (a) Rosenfield, R. E., Jr.; Parthasarathy, R.; Dunitz, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 4860–4862. (b) GuruRow, T. N.; Parthasarathy, R. *J. Am. Chem. Soc.* **1981**, *103*, 477–479. (c) Ramasubbu, N.; Parthasarathy, R.; Murray-Rust, P. *J. Am. Chem. Soc.* **1986**, *108*, 4308–4314. (d) Ramasubbu, N.; Parthasarathy, R. *Phosphorus Sulfur* **1987**, *31*, 221–229.

(5) Dunitz, J. D. *Philos. Trans. R. Soc. London* **1975**, *B272*, 99–108.

(6) Fukui, K.; Yonezawa, T.; Shinga, H. *J. Chem. Phys.* **1952**, *20*, 722–772.

(7) Sakurai, T.; Sundaralingam, M.; Jeffrey, G. A. *Acta Crystallogr.* **1963**, *16*, 354–363. These authors have noted earlier the two preferred geometries for the halogen···halogen contacts and have also pointed out the two types of interpretation for explaining the geometry.

(8) Williams, D. E.; Hsu, L. Y. *Acta Crystallogr.* **1985**, *A41*, 296–301.

(9) Nyburg, S. C.; Wong-Ng, W. *Proc. R. Soc. London* **1979**, *A367*, 29–45. Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr.* **1985**, *B41*, 274–279. Price, S. L.; Stone, A. J. *Mol. Phys.* **1982**, 1457–1470. Price, S. L.; Stone, A. J. *J. Phys. Chem.* **1988**, *92*, 3325–3335.

(10) Jando, K. C.; Klemperer, W.; Novick, S. E. *J. Chem. Phys.* **1976**, *64*, 2698–2699. Harris, S. J.; Novick, S. E.; Winn, J. S.; Klemperer, W. *J. Chem. Phys.* **1974**, *61*, 3866–3867.

(11) Umeyama, H.; Morokuma, K.; Yambe, S. *J. Am. Chem. Soc.* **1977**, *99*, 330–343.

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