no longer claim that the observed intensity ratio is inconsistent with a delocalized ground state. If indeed the ground state is delocalized we can conclude from Figure 8 that J' is in the range 0–0.07 eV.

It is interesting to note that eq 11 and 12 provide, in principle, a method for determining both the ground- and excited-state coupling integrals from XPS binding energies. Thus, we may write

$$J = \frac{1}{2}(E_1 + E_2) \tag{19}$$

and

$$J' = \frac{1}{2}[(E_2 - E_1)^2 - \Delta'^2]^{1/2} \tag{20}$$

Unfortunately, to obtain reliable values for the coupling integrals from eq 19 and 20 would require absolute binding energies considerably more accurate than can be measured from irradiated insulators.[18,19] A realistic estimate of such binding energy accuracies is at least ±0.1–0.2 eV for a given measurement. Since this uncertainty enters eq 19 and 20 via both the measurements on the mixed valence compound and also the reference compounds used to establish the energy zero for E_1 and E_2 and to obtain Δ', it is clear that these equations cannot, in practice, be used to estimate J and J' for a weakly coupled insulator.

We may summarize our conclusions as follows. A mixed valence dimer with a delocalized ground state (class III complex)

but relatively weak metal–metal interaction will have an X-ray photoemission spectrum indistinguishable from a class II complex. The nature of the ground state of the Creutz–Taube mixed valence dimer therefore cannot be decided from XPS measurements. Hush's model in its original form[7] led to a similar conclusion, but suggested that careful relative XPS peak intensity measurements would permit the two cases to be distinguished. We have shown that the Hush model must be modified to allow for the expected large difference in electron coupling in the ground and photoionized states. When this is done it is found that a class III dimer with relatively weak metal–metal interaction should always give two photoemission peaks with 1:1 intensity; relative intensity measurements therefore cannot distinguish this case from a class II dimer. Binding energies, although they are related to the coupling in both the ground and photoionized states, also cannot be used to evaluate the coupling because of inherent limitations on the accuracy with which they can be measured in an insulator.

Finally, we wish to note that the basic idea of the Hush model, namely, the localization of a delocalized ground state by core hole polarization in the photoionized state, is anticipated in the work of Friedel[27] and of Combescott and Nozieres[28] on metals. These authors show that core hole polarization in the photoionized state can cause an electron from the conduction band to become localized in a level below the band. This theory has been used to account, at least qualitatively, for unexpected splittings in the XPS of metallic sodium tungsten bronzes.[29]

(26) Orbital contraction in the photoionized state should greatly reduce the interaction between the two Ru atoms. In this connection we note that magnetic susceptibility measurements on the [III,III] dimer show that coupling between the two Ru(III) centers is negligible;[11] we would expect that the coupling between the two metal atoms in the photoionized state is even smaller than the Ru(III)–Ru(III) coupling.

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Conformational Analysis of Polysubstituted Ethanes

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Abstract: Empirical force field (EFF) calculations were performed for a number of polyarylsubstituted ethanes and the ground state geometry and strain energy were obtained. Optimal geometrical parameters are compared with experimental data from X-ray crystal-structure determination. The agreement is extremely good for bond lengths and bond angles. Significant discrepancies may occur for dihedral angles, probably due to the effect of packing forces in the crystalline phase.

The empirical force field method has become a quite reliable and widely accepted tool for the determination of structure and energy of organic molecules, specially hydrocarbons. Its merit and drawbacks and the limit of applicability have been reviewed and discussed many times.[1] Recently particular attention has been paid to arylethanes, and molecular mechanics has been extensively used in the static and dynamic analysis of the stereochemistry of a number of members of the family.[2] One of the most interesting results from the theory is the ground state ge-

ometry of the molecules under study and perhaps the most reliable test for the adopted potential and parametrization is the comparison with the geometry obtained by experiment of some kind. The size of the molecules considered here is such that the source of experimental data is almost completely restricted to X-ray diffraction.

Particular attention must be taken here since the calculations refer to an isolated molecule, while X-ray data describe the molecules packed in the crystal. The comparison is particularly meaningful when packing is not too tight, that is not too many intermolecular distances fall below the sum of the van der Waals radii, and when the molecule is "rigid". The definition of rigidity should be related to a complete normal mode analysis for the isolated molecules and to a lattice dynamics study of the crystal.[3] In rigid molecules vibrational frequencies for internal modes should

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be almost unaffected on going from the gas to the crystalline phase, and the internal and lattice frequencies should belong to two well-separated ranges. However, since such analyses are not available for the molecules and crystals to be considered here, we shall be content to define as rigid molecules those lacking single bonds around which rotation can easily occur due to the presence of multiple bonding and/or rings.

As an example, both requirements are met in a number of bridged annulenes, for which indeed molecular mechanics "predictions" are in excellent agreement with experimental findings.[4] In the case of polysubstituted ethanes in general, and polyarylethanes in particular, rather easy rotation around the central carbon–carbon bond and the carbon–carbon bonds connecting each substituent with the ethane fragment is to be expected and reasonable disagreement between calculated and experimental values of the relevant geometrical parameters cannot be taken as a failure of the theoretical method. In fact some discrepancies of the kind mentioned above have been found in the case of pentaphenylethane,[2c,e] where the theoretical ring twists and central ethane dihedral angles are somewhat different from the values obtained by X-ray diffraction.[5] Since experimental data for the number of related molecules are now available (see below), a complementary study of the same molecules by the empirical force field method seems to be appropriate at the present time. In this paper we report the results for 9,9′-bifluorenyl (1), 9-*tert*-butyl-9-(9′-fluorenyl)fluorene (2), 1,1,1-triphenylethane (3), and 1,1,1,2-tetraphenylethane (4).

Method of Calculation

The program of Schleyer, Andose, and Mislow was used,[6] with the choice of the pattern search minimization procedure with a consistency test of 0.01 kcal/mol on the total strain energy. Standard deviations in bond lengths and angles were always within ±0.002 Å and ±0.1°, respectively.
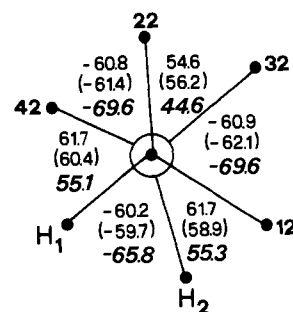
For molecules 3 and 4 the potential described by Andose and Mislow[7] was used as included in the program. For molecules 1 and 2 containing biphenyl subsystems, rather than following the procedure suggested by Mislow et al.[2c] where an "ad hoc" parametrization was introduced we used the Allinger and Sprague[8] force field, tailored to deal with conjugated systems, as modified by us.[9] Namely the stretching force constant and the equilibrium bond length for the C_{ar}–C_{ar} bond were given by k (mdyn/Å) = $5.0 + 3.975p$ and r_0 (Å) = $1.511 - 0.1815p$, where p is the relevant bond order obtained by a quantum-mechanical VESCF π-electron calculation.[10] The twist energy around the same bond was given by

$$E \text{ (kcal/mol)} = -19.72p \exp\frac{0.86r}{1.332(1-p)}\left(\frac{1.332}{r}\right)^{2.78}(\cos 2\omega - 1)$$

where ω is the angle of twist around the bond of order p and length r.

Results

9,9′-Bifluorenyl. This molecule is an example of back-clamped polyphenylethane,[2c] and two conformations compete for the ground-state geometry, namely the gauche and anti form. Force-field calculations had been performed for this molecule and the gauche structure with C_2 symmetry was found to be more stable by 6.6 kcal/mol with a C_{sp_3}–C_{sp_3} distance of 1.543 Å, to be compared with a value of 1.551 for the anti structure.[2c] Ex-

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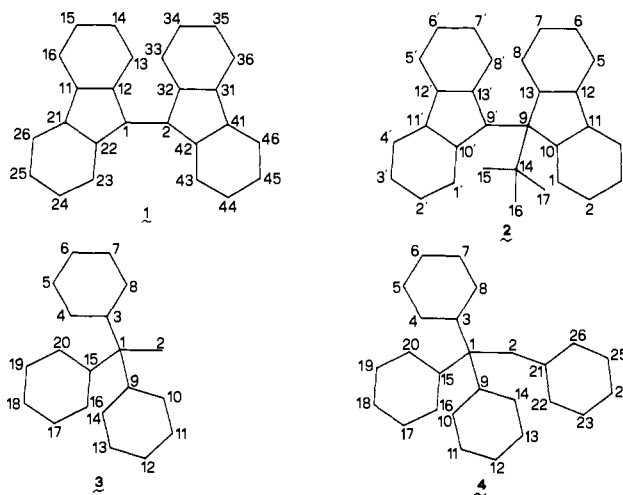(10) N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, **87**, 2081 (1965).

Figure 1. Dihedral angles (deg) for **1**. Additional values are [experimental values in parentheses; values from ref 2d in italics]: C_2–C_1–C_{12}–C_{13} -61.3° (-55.7), -62.2; C_2–C_1–C_{22}–C_{23} 62.4 (60.4), 64.3.
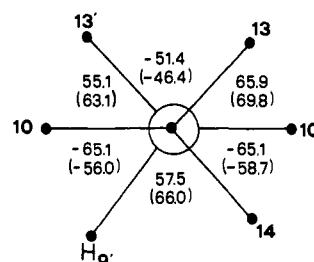
Figure 2. Dihedral angles (deg) for **2**. Additional values are [experimental values in parentheses]: C_9–$C_{9'}$–$C_{10'}$–C_{11} 68.0 (72.9); $C_{9'}$–C_9–$C_{13'}$–$C_{8'}$ -65.3 (-60.7).

Chart I

tended Hückel calculations have confirmed the first geometry to be favoured by 10.7 kcal/mol.[2c] A crystal structure determination has found that in the crystal the molecule has gauche conformation with C_2 symmetry.[2d] Our calculations are in line with all these previous results, the difference between the two conformations amounting now to 7.1 kcal/mol in energy and to 0.011 Å in the central bond length. Our and previous results are collected in Table I (bond lengths and bond angles)[11] and in Figure 1 (dihedral angles). Numbering of carbon atoms for all molecules is shown in Chart I. Geometrical parameters for conformations other than the ground state for molecules considered in the present paper are available from the authors on request.

9-*tert*-Butyl-9-(9′-fluorenyl)fluorene. For this molecule four different conformations have been considered: A, B, C, and D. In A, B, and C hydrogen $H_{9'}$ is gauche, anti, or eclipsed to carbon 14, respectively. In D $H_{9'}$ is eclipsed to C_{10}. The strain energy for the four minima are 24.0, 32.3, 31.9, and 30.4 kcal/mol, respectively. The geometrical parameters for the ground-state structure are shown in Table II (bond lengths and bond angles)[11]

(11) Supplementary material available.

Table III. Strain Energies (kcal/mol) for Structures
A, B, and C of Compound 3

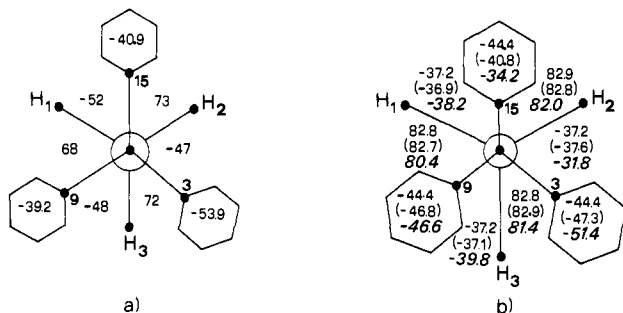| strain energy	A	B	C
stretching	3.03	3.05	3.13
bending	3.09	3.14	3.24
twist	0.56	0.51	0.51
nonbonded	8.12	8.18	8.05
out of plane	0.21	0.20	0.19
stretch-bend	−0.30	−0.28	−0.36
total	14.71	14.80	14.76

Figure 3. Dihedral angles (deg) for **3**: (a) experiment; (b) present work [A, B (in parentheses); C (italics)].

and Figure 2 (dihedral angles), in comparison with experimental data from a recent X-ray structure determination.[12]

1,1,1-Triphenylethane. For this molecule an experimental geometry is available.[13] Different minima have been obtained by starting from different inputs. Three minima, which we call A, B, and C, are particularly close in energy and a choice between them seems to be rather difficult since energy differences fall within the reliability limit of the method. Structure A was obtained starting from a modified experimental geometry in which a ternary symmetry was imposed. Such symmetry was spontaneously maintained during the minimization procedure. Structure B and C were obtained starting from the experimental geometry with full relaxation except that rotation was not allowed to one of the phenyl rings (the closest and the farthest with respect to the eclipsed position, respectively). In Table III the total strain energies and the different components are shown for the three structures. For the geometry of the three energy minima an EH calculation was carried out, and again the total energy turned out to be almost equal. According to these calculations structure C is the most stable one, with structure B and A lying 0.05 and 0.18 kcal/mol above. The calculated geometrical parameters are shown in Table IV (bond lengths and bond angles)[11] and in Figure 3 (dihedral angles) together with experimental results.

1,1,2-Tetraphenylethane. A number of different starting geometries have been considered in which all or part of the information from an X-ray crystal-structure determination[14] was incorporated. Most of these inputs lead to the same minimum, which turns out to be the absolute minimum. The parameters for the optimal geometry are reported in Table V (bond lengths and bond angles)[11] and in Figure 4 (dihedral angles). The strain energy at the minimum is 15.85 kcal/mol.

Discussion

A number of experimental determinations of the geometry of polyarylethanes became available in recent years[2d,5,12-14] and a comparison with results from EFF calculations seems to be appropriate at this stage. In order to be able to use in addition to the present results data already in the literature,[2] where a strain
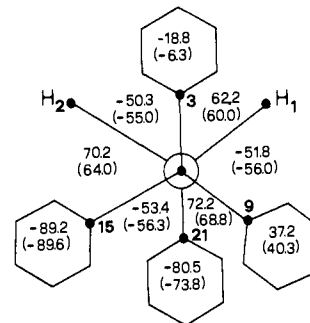
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Figure 4. Calculated and experimental (in parentheses) dihedral angles (deg) for **4**.

Table VI. Calculated and Experimental Central
C-C Bond Lengths (Å)

compound	exptl	calcd[2c]	present work
1, 9,9'-bifluorenyl	1.542[2d]	1.543	1.545
2, 9-*tert*-butyl-9-(9'-fluorenyl)fluorene	1.585[12]		1.572
3, 1,1,1-triphenylethane	1.553[13]		1.560
4, 1,1,1,2-tetraphenylethane	1.567[14]		1.571
5, 1,1,2,2-tetraphenylethane	1.540[15]	1.556	
6, pentaphenylethane	1.606[5]	1.595	
7, hexaphenylethane		1.639	

energy program different in some details was used, we recalculated compound **1**, for which both X-ray and EFF structural parameters were available.[2d] It can be seen from Table I and Figure 1 that the agreement between the two calculations is more than satisfactory, no difference in bond lengths and bond angles exceeding 0.01 Å or 2°, respectively.

The central dihedral angles are less close, with a maximum difference amounting up to 10°, while the ring rotations are again within the 2° limit. The behavior of dihedral angles will be further discussed (see below). The results for the "overlapping" compound **1** prompted us to use both our and Mislow's results in the discussion of experimental data. The most important structural feature in this class of compounds is the length of the central bond.

In Table VI theoretical and experimental values are collected for the interesting molecules. We have included all the molecules for which experimental data are available plus hexaphenylethane (**7**). Besides the excellent agreement between the two calculated values for **1**, it is gratifying to notice that in our calculations only for one molecule does the difference $r_{exp} - r_{calcd}$ exceeds 0.01 Å, namely 0.013 Å for **2**. Other important geometrical features are the bond angles at the tetrahedral carbon. In **1** both ends of the ethane fragments are heavily substituted (two phenyl rings are bonded to each end) and strain is revealed mainly by a decrease (with respect to the regular tetrahedral value) of the bond angles $C_{ph}-C_{eth}-C_{ph}$ with a corresponding increase of the angles $C_{eth}-C_{eth}-C_{ph}$. This is true also for **2** on the side carrying the hydrogen atom (carbon 9'), while at carbon 9 the presence of the tertiary butyl group changes the situation and there is a large C(9')−C(9)−C(14) value to decrease the front interaction of the butyl group and a small C(10)−C(9)−C(13) value to decrease its back interaction.

The tertiary butyl group tries to decrease its bulkiness by decreasing the internal bond angles. The tetrahedral situation is closely maintained at C_1 in **3**, while in **4** at carbon 1 the ring facing the two hydrogens is front displaced while at carbon 2 the isolated phenyl is back displaced. The above discussion can nicely be based on the experimental or calculated numbers.

Now we turn to the central dihedral angle, $C_{ph}-C_{eth}-C_{eth}-C_{ph}$, and the rotation angles of the phenyl rings. As was pointed out previously this is the most delicate point, since the potentials for rotations around the single bond usually are rather shallow with small energy barriers. Here small errors in the evaluation of the potential produce large variations in the rotational angles. From the values in Figures 1-4 it can be noticed however that when

the rotation potential is made steeper by ring clamping (compounds **1** and **2**) the agreement between calculated and experimental ring dihedral values improves significantly with respect to the unclamped situation. For all molecules the conformation around the central bond can always be described as approximately staggered. No geometrical parameters are reported in this paper for the phenyl rings. All the rings show slight distorsion with respect to hexagon symmetry. For unclamped rings the internal bond angle at the carbon connected to the ethane fragment is always calculated and found to be smaller than 120°, by a few degrees. The data are available from the authors, upon request. From the body of the results the general conclusion can be drawn that the EFF method is very reliable in the prediction of geometry for polyarylethylenes, giving support to the argument put forward by Mislow.[2] In fact, the average errors turned out to be 1.0% in bond lengths and 1.3% in bond angles.

The weakest points are the torsion around the central bond and the ring rotations. However, it must be remembered here that X-ray data describe the molecules packed in the crystal. Intermolecular forces come into play which may cause considerable change of these angles even when intermolecular atom–atom distances fall in the normal range. The suggestion can be made here that nonbonded intermolecular interactions should be included. Indeed preliminary calculations along these lines point in the right direction but for quantitative agreement an "ad hoc" parameterization of nonbonded intermolecular interactions, at variance with nonbonded intramolecular ones, should be performed. Work along these lines is actually in progress.

The Relationship between Nuclear Quadrupole Coupling Constants and the Asymmetry Parameter. The Interplay of Theory and Experiment

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Abstract: A diagrammatic scheme is proposed for correlating assignments and orientations of the electric field gradient (EFG) components of nuclei in molecules. It is illustrated for oxygen in organic compounds and relies on an ordered, although not necessarily linear, relationship between ^{17}O nuclear quadrupole coupling constants and the asymmetry parameter recently noted for hydroxyl and carbonyl groups. All the available ^{17}O data from ab initio EFG calculations and NQR experiments on organic compounds are surveyed and integrated. The relative magnitudes of perturbations to the oxygen EFG components from differing substituents, intermolecular forces such as H bonding, and crystal lattice field effects are analyzed. Particular attention is given to correlating the EFG assignments and orientations of oxygen in the carboxyl and hydroxyl groups of carboxylic acids as, through increasing strength of H bonding, they become chemically equivalent in the limit of symmetrical H bonding as represented here by type A acid salts.

Introduction

The electric field gradients (EFG's) around nuclei in molecules have been shown by both theoretical[1–5] and experimental (chiefly NQR[6–8]) methods to be very sensitive to the chemical and physical environment of the nucleus, and hence their determination offers considerable potential to the chemist for studying bonding in compounds containing a given nucleus—for example, H, N, or O—in different functional groups or for varying substituents etc. This potential is hampered at present by problems in the extraction of complete EFG information from the available experimental data: specifically, it is difficult in many cases to establish the assignments and orientations of the EFG tensor with respect to molecular axes from NQR results. While quantum mechanical calculations can readily provide the assignments and orientations, the accuracy of the calculated coupling amplitudes is much less than can be obtained routinely by experiment. Few EFG results from gas phase (microwave spectroscopy) or liquid phase (NMR) are available, and hence separation of contributions to the measured solid-phase EFG's from intermolecular interactions such as H bonding and crystal-lattice perturbations is an additional problem.

Consequently the object of this paper is to propose a regime which utilizes the limited number of theoretical and gas-phase results in compiling graphs to correlate and analyze experimental data for the solid state: this procedure is illustrated for organic oxygen-containing compounds although it is expected to be applicable to other nuclei of major chemical interest such as nitrogen. The paper builds upon recent proposals of the existence of a

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