Figure 1. A view of the molecule with some bond lengths and angles of interest. Deviation of individual atoms from their mean plane are Pt, 0.004; P(1), −0.004; P(2), 0.005; C(carb), 0.002; and C, −0.007 Å.
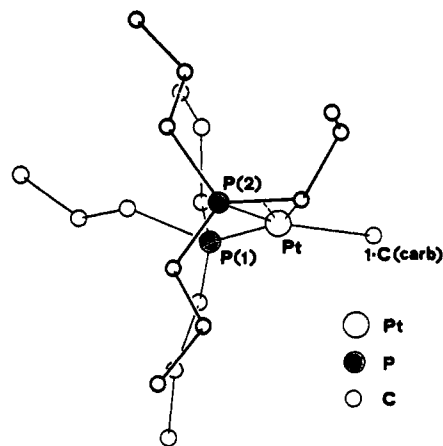

Figure 2. A sketch showing the geometrical relation between the coordination plane and the phosphine ligand bonded to Pt atom through its P and C atoms. Only the coordinated carborane atom is shown.

adjacent to the coordinated carbon atom are nearly equidistant from Pt (from 3.31 (2) to 3.43 (2) Å); (ii) the internal metallation involving one alkyl group of the phosphine ligand. However such a metallation does not lead to four- or five-membered rings but involves the n-propyl carbon atom bonded to the P atom. Such a three-membered cycle was already postulated by Chatt and Davidson[6] for the $[(Me_2P)_2CH_2CH_2]_2Ru(0)$.

The geometry of the PtP(2)C cycle may be described by assuming either two Pt–C and Pt–P σ bonds or a π-olefin-like bond between Pt and a P=C double bond. A careful examination shows bond lengths and angles to be in better agreement with the latter bonding scheme. In fact the P(2)–C distance of 1.76 (2) Å is shorter than the other P–C distances which range from 1.82 (2) to 1.89 (2) Å and suggests a significant amount of double bond character. Furthermore the sum of the angles CPC is 342° around P(2) and 308° around P(1). The nonhydrogen atoms of the [(–CH₂)₂P=CHCH₂–] group are almost coplanar. Their mean plane is nearly perpendicular to the coordination plane (see Figure 2). The Pt–P(1) bond length of 2.286 (5) Å appears quite normal for Pt^{II} square planar complexes.[7] On the other hand, the Pt–P(2) bond length (2.202 (5) Å) is shorter, but it does not dramatically differ from the value reported for Pt–P-n-Pr₃ distances,[8] which range from 2.230 (9) to 2.262 (4) Å. Furthermore, the kind of the bonding of P(1) and P(2) to Pt and their geometries are substantially different. So any comparison of bond lengths may be unreliable.

As far as the n-propyl groups are concerned, they have a nearly trans conformation, with the exception of

that involved in the coordination to the metal. In this case the conformation is nearly gauche, the torsion angle being 100.6°, probably due to the steric hindrance of the bulky carboranyl ligand.

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On the Blue Shift of the n → π* Band of Acetone in Water

Sir:

One of the more dramatic effects of hydrogen bonding is the well-known "blue shift" of the n → π* band, observed when a molecule possessing an n → π* transition is placed in a hydrogen-bonding solvent. In recent ab initio studies of hydrogen bonding between water and formaldehyde, it was found that the calculated energy of the n → π* transition in the water–formaldehyde dimer is greater than it is in the monomer, thus reproducing qualitatively the observed blue shift.[1,2]

In their study of the water–formaldehyde system, Iwata and Morokuma noted that the calculated blue shift in the water–formaldehyde trimer is in rather good agreement with the experimental blue shift of the n → π* band of acetone in water. This comparison was interpreted by them as support for the existence of a water–acetone trimer in solution, with the acetone molecule hydrogen bonded at the carbonyl oxygen to two water molecules.[1] A more direct comparison of experimental and theoretical data for the blue shift has not heretofore been possible, due to the experimental difficulties associated with the water–formaldehyde system and the lack of theoretical studies on systems for which experimental data are available.

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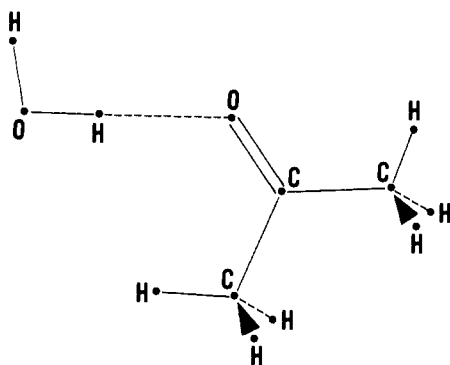(2) J. E. Del Bene, J. Amer. Chem. Soc., 95, 6517 (1973).

Figure 1. The water–acetone dimer.

In the course of a continuing study of the carbonyl group as a proton acceptor, the water–acetone system has been investigated, and the optimized structure of the water–acetone dimer determined. The n → π* transition energies in acetone, the water–acetone dimer, and a water–acetone trimer have also been calculated. These results now permit a direct comparison of theoretical and experimental values for the blue shift of the n → π* band. It is the purpose of this communication to present this comparison and to interpret the results in light of previous discussions of n → π* transitions in dimers.

The *ab initio* SCF calculations which have been performed employed the minimal STO-3G basis set with standard scale factors.[3] The optimized geometry of acetone was first determined, and held rigid for all dimer calculations. The procedure followed for optimizing the ground state structure of the dimer is given in a previous paper.[4] The optimized dimer, shown in Figure 1, has C_s symmetry, an intermolecular O–O distance of 2.84 Å, a linear O–H···O hydrogen bond, and an angle of 125° between the intermolecular O–O line and the C–O bond. The calculated intermolecular energy (hydrogen bond energy) is −0.00671 au. A thorough discussion of this dimer will be included in a future publication.

The vertical n → π* transition energies in acetone, the water–acetone dimer, and a water–acetone trimer were calculated using the configuration interaction (CI) method. The trimer, in which the carbonyl oxygen is hydrogen bonded to two water molecules, was constructed from the optimized dimer with the restriction of C_{2v} symmetry.[5] For monomer, dimer, and trimer, limited first-order CI functions were obtained consisting of linear combinations of 90 singly excited functions. The transition energies resulting from the CI calculations are given in Table I.

From Table I, it is evident that the calculated and experimental n → π* transition energies of acetone are in very good agreement. Moreover, the experimental n → π* transition energy of acetone in water is also in agreement with the calculated transition energy in the water–acetone dimer. Thus, the experimental blue shift of 0.19 eV of the n → π* band of acetone in water is

reproduced by the calculated blue shift of 0.18 eV in going from monomer to hydrogen-bonded dimer. On the other hand, the calculated transition energy in the trimer corresponds to a blue shift of 0.30 eV, which is greater than the experimental value. Although the calculations refer more directly to the gas phase, the above comparisons do support the existence of a water–acetone dimer, rather than the proposed trimer, in solutions of acetone in water.

Also evident in Table I is a correlation between the calculated n → π* transition energies in the dimer and trimer and the hydrogen bond strengths in these species. In particular, these transition energies are approximated to within 0.02 eV, as the sum of the monomer n → π* transition energy and the hydrogen bond strength in the corresponding polymer. This correlation has been observed previously in hydrogen-bonded dimers and interpreted as indicating that the blue shift reflects the additional energy required to break the hydrogen bond upon excitation to the dimer excited state.[6]

In summary, the direct comparison of theoretical and experimental n → π* transition energies of acetone and acetone in water does not support the suggestion that the acetone molecule in solution is hydrogen bonded to two water molecules. Rather, the interpretation consistent with the data obtained in this study is that the acetone molecule tends to hydrogen bond to a single water molecule. The blue shift of the n → π* band then reflects the additional energy required to break the hydrogen bond in the excited state of the dimer.

Table I. Hydrogen Bond and n → π* Transition Energies

	Hydrogen bond energy (eV)	n → π* transition energy (eV)	Experimental n → π* transition energy[a] (eV)
Monomer		4.48	4.49[b]
Dimer	0.18	4.66	4.68[c]
Trimer	0.32	4.78	

[a] Experimental data are λ_{max} values, taken from C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Plenum Press, New York, N. Y., 1967. [b] n → π* energy of acetone in heptane. [c] n → π* energy of acetone in water.

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(5) Full optimization of a water–formaldehyde trimer with C_{2v} symmetry was found to lead to only a slight additional stabilization of the trimer. The n → π* transition energies in the trimer constructed from the optimized dimer and in the optimized trimer were equal to within 0.01 eV.

(6) See ref 2, and references cited therein.

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Photolysis of Cyclobutyl Aryl Ketones. Evidence for the Involvement of an Excited State Conformational Equilibrium in Their Photoconversion to Aryl Bicyclo[1.1.1]pentanols

Sir:

A great deal of recent research on small ring compounds has focused on bicyclo[1.1.1]pentanes.[1,2] Among the synthetic entries[3] into the ring system, the

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