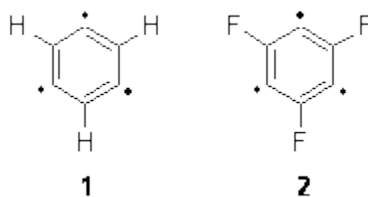


TRIDEHYDROBENZENE

In section 4.4 of the book, I discuss in great detail the computational (and some experimental) studies of the benzyne, the formal diradicals created by loss of two hydrogen atoms from benzene. Now comes a very nice experimental study on a molecule that takes the next step: 1,3,5-tridehydrobenzene **1**, benzene that lacks three hydrogen atoms. Sander reports the preparation and characterization of trifluoro-1,3,5-tridehydrobenzene **2**.¹ The characterization of this novel molecule is made through comparison with computed IR spectra.



2 is prepared by flash vapor pyrolysis of 1,3,5-triiodo-2,4,6-trifluorobenzene and then trapping the products in a low temperature matrix. Sander identifies five IR peaks of a product he believes is **2**. These IR frequencies are listed in Table 1.

Table 1. Experimental and computed^a IR frequencies (cm⁻¹) and relative intensities of **2**.

Expt		2a		2b ^b	
ν	I	ν	I	ν	I
954	60	921.7	57	976.2	57
1030	30	997.6	54	1016.0	55
1266	40	1221.8	35	1291.3	33
		1310.6	16	1325.4	30
1560	70	1530.0	73	1572.6	100
1738	100	1726.6	100	1690.6	88

^aUBLYP/cc-pVTZ. ^bTransition state.

In order to confirm that this IR spectra comes from **2**, Sander computed the structure and IR frequencies of both **1** and **2**. The ²A₁ structure of **1** had been studied previously², but what had gone unnoticed is that another structure is possible, the ²B₂ state. These two states differ in the separation between C₁ and C₃. When the distance is short, the SOMO is of a₁ symmetry and this orbital has bonding character between these two carbon centers, giving rise to the ²A₁ state (**1a**). As the distance gets longer between C₁ and C₃, a b₂ orbital, having antibonding character between C₁ and C₃, becomes lower in energy than the a₁ orbital, so that the structure is ²B₂ (**1b**).

The UBLYP/cc-pVTZ optimized structures are shown in Figure 1. **1a** is 2-3 kcal mol⁻¹ lower in energy than **1b**. Furthermore, **1b** has one imaginary frequency and is not a local energy minimum. Sander also optimized the structures of **2a** and **2b**, finding little effect due to the fluorine substitution.

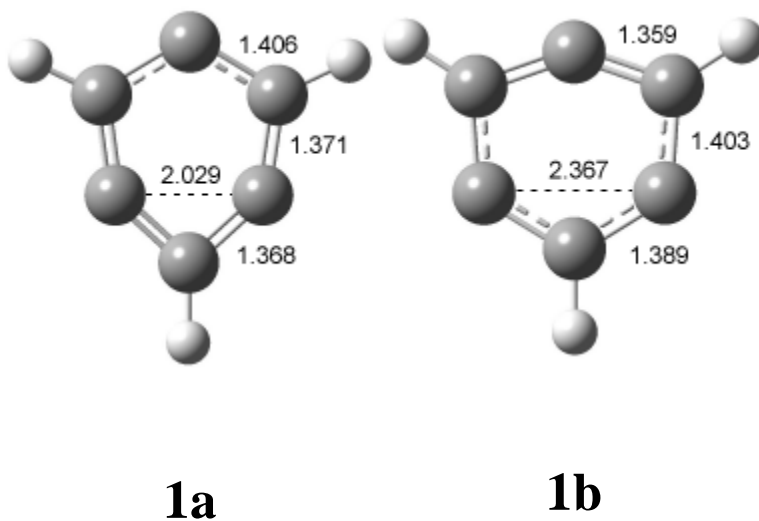


Figure 1. UBLYP/cc-pVTZ optimized structures of **1a** (²A₁) and **1b** (²B₁).

The computed IR frequencies are listed in Table 1. The computed frequencies (and their relative intensities) of **2a** match up strikingly well with those of the experiment. Sander concludes that **2a** has in fact been prepared and characterized.

Source: <http://comporgchem.com/blog/?p=28>