Self-Consistent-Field Studies of the Electronic Structures of Cyclopropane and Benzene

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Abstract: Accurate SCF wave functions employing optimized minimum basis sets of Slater-type orbitals are presented for cyclopropane and benzene. Atomization energies and ionization potentials are calculated and compared with experiment. The energies of the $1e_{1g} \rightarrow 1e_{2u}$ ($\pi \rightarrow \pi^*$) spectroscopic transitions in benzene are approximated using the $1e_{2u}$ virtual orbital. Calculations of the diamagnetic susceptibility of benzene yield an anisotropy of reasonable value. Plots of calculated electron density are used to illustrate the nature of bent bonding in cyclopropane and σ–π interpenetration in benzene.

The interpretation of the unusual physical and chemical properties of cyclopropane and benzene has been a long-standing challenge to experimental and theoretical chemists. In this paper the results of self-consistent-field (SCF) calculations for these two molecules are reported, and these *ab initio* results are utilized to discuss bonding and other properties in cyclopropane and benzene.

Optimized minimum Slater basis sets have been previously reported for CH_4,[1] C_2H_2 and C_2H_4,[2a] and C_2H_6.[2b] The results given here therefore represent an extension of this work to larger and more complex systems. Although several larger Gaussian basis sets have been reported for both cyclopropane and benzene,[3] our results are the first obtained from an optimized Slater basis set. Our Slater wave functions thus provide a useful comparison with previous Gaussian calculations, in addition to affording the advantage of relative ease in chemical interpretation and transferability of orbital properties. Because the C–C bonds in benzene and cyclopropane represent two extreme examples of binding in cyclic hydrocarbons, our results will hopefully be of further use in both nonempirical and semiempirical studies of related molecules, in addition to providing useful comparisons with previous calculations on hydrocarbons.[1,2]

Calculations

Wave functions for cyclopropane and benzene were determined by the SCF–LCAO method of Roothaan[4] using computer programs described elsewhere.[2] The atomic coordinates and numbering system used in these calculations are given in Table I. The cyclopropane calculation utilized the full D_{3h} molecular symmetry. In the benzene calculation it was found most economical to employ D_{3h} symmetry, although the molecular geometry displays the full D_{6h} symmetry. Because of this use of reduced symmetry, each of the nearly degenerate inner-shell orbitals (molecular orbitals 1–6) does not display the full molecular symmetry. These slight nonequivalences have no effect on any molecular property, since summation over the inner-shell orbitals gives fully symmetric results.

Table I. Geometry of Cyclopropane and Benzene (au)

	x	*y*	*z*
		C_3H_6	
1H/4H	2.67377	0.0000	+1.75110
2H/5H	−1.33688	2.31555	±1.75110
3H/6H	−1.33688	−2.31555	±1.75110
1C	1.66277	0.00000	0.00000
2C	−0.83138	1.44000	0.00000
3C	−0.83138	−1.44000	0.00000
		C_6H_6	
1H/4H	±4.68661	0.00000	0.0
2H/5H	±2.34331	±4.05872	0.0
3H/6H	±2.34331	±4.05872	0.0
1C/4C	±2.63622	0.00000	0.0
2C/5C	±1.31811	±2.28303	0.0
3C/6C	±1.31811	±2.28303	0.0

Both calculations used minimum basis sets of Slater-type orbitals. Earlier experience with hydrocarbons[2] showed that the carbon 2p and hydrogen 1s orbital exponents were the ones most strongly coupled to the molecular energy. Thus both of these orbital exponents were reoptimized for each molecule. The C 1s and C 2s exponents were estimated from optimized minimum basis set calculations on small molecules.[2] The optimization of the C 2p exponents is especially important, since in a minimum basis set the coefficients of certain of the components (*e.g.*, $2p_z$ in benzene) are completely determined by symmetry. A more complete basis set for cyclopropane or benzene would allow for anisotropy in the 2p orbitals.[2a] The final orbital exponents are listed in Table II.

Table II. Exponents for Basis Orbitals

	C_3H_6	C_6H_6
H 1s	1.2096	1.2264
C 1s	5.68	5.68
C 2s	1.74	1.75
C 2p	1.7118	1.6917

In each of the calculations the integrals over atomic basis orbitals were calculated to an accuracy of 1 × 10^{-5} au. All computations were performed on an

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Table III. Eigenvalues and Eigenvectors for Cyclopropane

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
	1 A'1	1 E'	1 E'	2 A'1	2 E'	2 E'	1 A"2	3 A'1	1 E"	1 E"	3 E'	3 E'	1 A'2	2 A"2	4 A'1	4 E'	4 E'	5 E'	5 E'	2 E"	2 E"
	-11.2033	-11.2030	-11.2030	-1.0933	-0.7921	-0.7921	-0.0598	-0.5834	-0.5049	-0.5049	-0.3805	-0.3805	0.4587	0.5800	0.0233	0.0049	0.0849	0.7263	0.7283	0.0501	0.0501
1H1S	-0.0028	-0.0038	0.0	0.0704	0.2385	0.0	0.1945	-0.1828	0.3801	0.0	0.1592	0.0	0.0	0.5239	0.5005	0.5830	0.0	0.4795	0.0	0.7403	0.0
2H1S	-0.0028	0.0019	-0.0033	0.0704	-0.1192	0.2005	0.1945	-0.1828	-0.1901	0.3292	-0.0790	0.1379	0.0	0.5239	0.5005	-0.2919	0.5050	-0.2398	0.4153	-0.3701	0.0411
3H1S	-0.0028	0.0019	0.9033	0.0704	-0.1192	-0.2005	0.1945	-0.1828	-0.1901	-0.3792	-0.0796	-0.1379	0.0	0.5239	0.5005	-0.2919	-0.5050	-0.2398	-0.4153	-0.3701	-0.0411
4H1S	-0.0020	-0.0038	0.0	0.0704	0.2385	0.0	-0.1945	-0.1828	-0.3801	0.0	0.1592	0.0	0.0	-0.5239	9.5005	0.5838	0.0	0.4795	0.0	-0.7403	0.0
5H1S	-0.0020	0.0019	-0.0033	0.0704	-0.1192	0.2005	-0.1945	-0.1828	0.1901	-0.3292	-0.0790	0.1379	0.0	-0.5239	0.5005	-0.2919	0.5050	-0.2398	0.4153	0.3701	-0.0411
6H1S	-0.0028	0.0019	0.0033	0.0704	-0.1192	-0.2005	-0.1945	-0.1828	0.1901	0.3292	-0.0790	-0.1379	0.0	-0.5239	0.5005	-0.2919	-0.5050	-0.2398	-0.4153	0.3701	0.6411
1C1S	0.5747	0.8122	0.0	-0.1301	-0.1041	0.0	0.0	0.0072	0.0	0.0	0.0154	0.0	0.0	0.0	0.0903	0.2120	0.0	-0.0175	0.0	0.0	0.0
2S	0.0104	0.0224	0.0	0.3532	0.5099	0.0	0.0	-0.0313	0.0	0.0	-0.1001	0.0	0.0	0.0	-0.0828	-1.3790	0.0	0.0723	0.0	0.0	0.0
2PZ	0.0	0.0	0.0	0.0	0.0	0.0	-0.3197	0.0	-0.4001	0.0	0.0	0.0	0.0	0.5711	0.0	0.0	0.0	0.0	0.0	1.0551	0.0
X	0.0015	-0.0027	0.0	-9.1101	0.1413	0.0	0.0	-0.3701	0.0	0.0	0.3240	0.0	0.0	0.0	-0.4000	0.2218	0.0	-1.1004	0.0	0.0	0.0
Y	0.0	0.0	-0.0020	0.0	0.0	0.1524	0.0	0.0	0.0	0.0	0.0	-0.0244	0.7503	0.0	0.0	0.0	0.3940	0.0	-0.3312	0.0	0.0
2C1S	0.5747	-0.4001	0.7033	-0.1301	0.0820	-0.1421	0.0	0.0072	0.0	0.0	-0.0077	0.0133	0.0	0.0	0.0903	-0.1003	0.1842	0.0088	-0.0152	0.0	9.0
2S	0.0104	-0.0112	0.0194	0.3532	-0.2549	0.4415	0.0	-0.0313	0.0	0.0	0.0501	-0.0807	0.0	0.0	-0.0828	0.0898	-1.1947	-0.0301	0.0020	0.0	0.0
2PZ	0.0	0.0	0.0	0.0	0.0	0.0	-0.3197	0.0	0.2331	-0.4037	0.0	0.0	0.0	0.5711	0.0	0.0	0.0	0.0	0.0	-0.5270	0.9130
X	-0.0007	-0.0020	0.0001	0.0581	0.1490	0.0048	0.0	0.1881	0.0	0.0	-0.3873	-0.4107	-0.0550	0.0	0.2003	0.3510	0.0745	-0.5250	0.3357	0.0	0.0
Y	0.0013	0.0001	-0.0027	-0.1000	0.0048	0.1441	0.0	-0.3257	0.0	0.0	-0.4107	0.0809	-0.3702	0.0	-0.3409	0.0745	0.2649	0.3357	-0.9126	0.0	0.0
3C1S	0.5747	-0.4001	-0.7033	-0.1301	0.0820	0.1421	0.0	0.0072	0.0	0.0	-0.0077	-0.0133	0.0	0.0	0.0903	-0.1003	-0.1042	0.0088	0.0152	0.0	0.0
2S	0.0104	-0.0112	-0.0194	0.3532	-0.2549	-0.4415	0.0	-0.0313	0.0	0.0	0.0501	0.0007	0.0	0.0	-0.0828	0.0898	1.1947	-0.0301	-0.0020	0.0	0.0
2PZ	0.0	0.0	0.0	0.0	0.0	0.0	-0.3197	0.0	9.2331	0.4037	0.0	0.0	0.0	0.5711	0.0	0.0	0.0	0.0	0.0	-0.5270	-0.9130
X	-0.0007	-0.0020	-0.0001	0.0581	0.1490	-0.0048	0.0	0.1881	0.0	0.0	-0.3073	0.4107	0.0550	0.0	0.2003	0.3510	-0.0745	-0.5250	-0.3357	0.0	0.0
Y	-0.0013	-0.0001	-0.0027	0.1000	-0.0048	0.1441	0.0	0.3257	0.0	0.0	0.4107	0.0009	-0.3702	0.0	0.3409	-0.0745	0.2649	-0.3357	-0.9120	0.0	0.0

Table IV. Eigenvalues and Eigenvectors for Benzene

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	1 A1G	1E1U	1E1U	1E2G	1E2G	1 B1U	2 A1G	2 E1U	2 E1U	2 E2G	2 E2G	3 A1G	2 B1U	1 B2U	3 E1U	3 E1U	1 A2U	3 E2G	3 E2G
	-11.2050	-11.2040	-11.2040	-11.2042	-11.2042	-11.2039	-1.1024	-0.9072	-0.9072	-0.7773	-0.7773	-0.0099	-0.0040	-0.5024	-0.5420	-0.5420	-0.4070	-0.4420	-0.4420
1H1S	0.0020	0.0027	0.0	0.0025	0.0	0.0017	0.0484	0.1105	0.0	-0.1000	0.0	0.1723	0.2335	0.0	-0.2702	0.0	0.0	0.2952	0.0
2H1S	0.0020	0.0013	-0.0023	-0.0013	0.0022	-0.0017	0.0404	0.0553	-0.0957	0.0903	-0.1504	0.1722	-0.2335	0.0	-0.1391	0.2410	0.0	-0.1470	0.2557
3H1S	0.0020	-0.0013	-0.0023	-0.0013	-0.0022	0.0017	0.0404	-0.0553	-0.0957	0.0903	0.1504	0.1723	0.2335	0.0	0.1391	0.2410	0.0	-0.1470	-0.2557
4H1S	0.0020	-0.0020	0.0	0.0025	0.0	-0.0017	0.0404	-0.1105	0.0	-0.1000	0.0	0.1722	-0.2335	0.0	0.2702	0.0	0.0	0.2952	0.0
5H1S	0.0020	-0.0013	0.0023	-0.0013	0.0022	0.0017	0.0404	-0.0553	0.0957	0.0903	-0.1504	0.1723	0.2335	0.0	0.1391	-0.2410	0.0	-0.1470	0.2557
6H1S	0.0020	0.0013	0.0023	-0.0013	-0.0022	-0.0017	0.0404	0.0553	0.0957	0.0903	0.1504	0.1722	-0.2335	0.0	-0.1391	-0.2410	0.0	-0.1470	-0.2557
1C1S	-0.4079	-0.5779	0.0	-0.5710	0.0	-0.4040	-0.1022	-0.1428	0.0	0.1111	0.0	-0.0003	-0.0031	0.0	-0.0257	0.0	0.0	0.0077	0.0
2S	-0.0001	-0.0113	0.0	-0.0102	0.0	-0.0134	0.2045	0.3919	0.0	-0.3223	0.0	0.0383	0.2039	0.0	0.0004	0.0	0.0	-0.0139	0.0
2PZ	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3317	0.0	0.0
X	-0.0011	-0.0004	0.0	0.0014	0.0	0.0019	-0.0020	-0.0294	0.0	-0.0881	0.0	0.2349	0.1715	0.0	-0.3705	0.0	0.0	0.2000	0.0
Y	0.0	0.0	0.0029	0.0	-0.0027	0.0	0.0	0.0	0.1305	0.0	0.2308	0.0	0.0	0.3312	0.0	0.1030	0.0	0.0	0.3330
2C1S	-0.4050	-0.2050	0.4947	0.2008	-0.5003	0.4075	-0.1022	-0.0714	0.1230	-0.0550	0.0902	-0.0003	0.0031	0.0	-0.0128	0.0222	0.0	-0.0039	0.0067
2S	-0.0000	-0.0050	0.0097	0.0082	-0.0141	0.0134	0.2045	0.1959	-0.3394	0.1011	-0.2791	0.0303	-0.2039	0.0	0.0402	-0.0097	0.0	0.0009	-0.0120
2PZ	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3317	0.0	0.0
X	-0.0005	0.0021	0.0015	0.0017	0.0018	-0.0009	-0.0313	0.0950	0.0718	-0.1550	-0.1407	0.1174	-0.0058	-0.2000	-0.0154	0.2050	0.0	-0.3212	-0.0203
Y	0.0010	0.0015	0.0004	0.0010	-0.0004	0.0010	0.0542	0.0718	0.0121	-0.1407	0.0009	-0.2034	0.1405	-0.1050	0.2050	-0.2521	0.0	-0.0203	-0.2977
3C1S	-0.4079	0.2090	0.5005	0.2855	0.4945	-0.4040	-0.1022	0.0714	0.1230	-0.0550	-0.0902	-0.0003	-0.0031	0.0	0.0128	0.0222	0.0	-0.0039	-0.0007
2S	-0.0001	0.0057	0.0098	0.0081	0.0140	-0.0134	0.2045	-0.1959	-0.3394	0.1011	0.2791	0.0383	0.2039	0.0	-0.0402	-0.0097	0.0	0.0009	0.0120
2PZ	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3317	0.0	0.0
X	0.0005	0.0021	-0.0014	-0.0017	0.0018	-0.0009	0.0313	0.0950	-0.0718	0.1556	-0.1407	-0.1174	-0.0058	0.2808	-0.0154	-0.2050	0.0	0.3212	-0.0203
Y	0.0009	-0.0014	0.0004	0.0018	0.0004	-0.0010	0.0542	-0.0718	0.0121	-0.1407	-0.0009	-0.2034	-0.1485	-0.1050	-0.2050	-0.2521	0.0	-0.0203	0.2977
4C1S	-0.4050	0.5712	0.0	-0.5777	0.0	0.4075	-0.1022	0.1428	0.0	0.1111	0.0	-0.0083	0.0031	0.0	0.0257	0.0	0.0	0.0077	0.0
2S	-0.0000	0.0112	0.0	-0.0103	0.0	0.0134	0.2045	-0.3919	0.0	-0.3223	0.0	0.0383	-0.2039	0.0	-0.0804	0.0	0.0	-0.0139	0.0
2PZ	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3317	0.0	0.0
X	0.0011	-0.0004	0.0	-0.0014	0.0	0.0019	0.0620	-0.0294	0.0	0.0881	0.0	-0.2349	0.1715	0.0	-0.3705	0.0	0.0	-0.2800	0.0
Y	0.0	0.0	0.0029	0.0	0.0027	0.0	0.0	0.0	0.1305	0.0	-0.2308	0.0	0.0	0.3312	0.0	0.1030	0.0	0.0	-0.3330
5C1S	-0.4079	0.2890	-0.5005	0.2055	-0.4945	-0.4040	-0.1022	0.0714	-0.1230	-0.0556	0.0902	-0.0003	-0.0031	0.0	0.0128	-0.0222	0.0	-0.0039	0.0007
2S	-0.0001	0.0057	-0.0098	0.0081	-0.0140	-0.0134	0.2045	-0.1959	0.3394	0.1011	-0.2791	0.0303	0.2039	0.0	-0.0402	0.0097	0.0	0.0069	-0.0120
2PZ	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3317	0.0	0.0
X	0.0005	0.0021	0.0014	-0.0017	-0.0018	-0.0009	0.0313	0.0950	0.0718	0.1556	0.1407	-0.1174	-0.0058	-0.2808	-0.0154	0.2050	0.0	0.3212	0.0203
Y	-0.0009	0.0014	0.0004	-0.0018	0.0004	0.0010	-0.0542	0.0718	0.0121	0.1407	-0.0069	0.2034	0.1485	-0.1050	0.2050	-0.2521	0.0	0.0203	0.2977
6C1S	-0.4050	-0.2850	-0.4947	0.2888	0.5003	0.4075	-0.1022	-0.0714	-0.1230	-0.0550	-0.0062	-0.0003	0.0031	0.0	-0.0128	-0.0222	0.0	-0.0039	-0.0007
2S	-0.0000	-0.0050	-0.0097	0.0082	0.0141	0.0134	0.2045	0.1959	0.3394	0.1611	0.2791	0.0383	-0.2039	0.0	0.0402	0.0097	0.0	0.0009	0.0120
2PZ	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3317	0.0	0.0
X	-0.0005	0.0021	-0.0015	0.0017	-0.0018	-0.0009	-0.0313	0.0950	-0.0718	-0.1550	0.1407	0.1174	-0.0050	0.2800	-0.0154	-0.2050	0.0	-0.3212	0.0203
Y	-0.0010	-0.0015	0.0004	-0.0018	-0.0004	-0.0010	-0.0542	-0.0718	0.0121	0.1407	0.0009	0.2034	-0.1485	-0.1050	-0.2050	-0.2521	0.0	0.0203	-0.2977

	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	1 E1G	1 E1G	1 E2U	1 E2U	1 B2G	4 A1G	4 E1U	4 E1U	3 B1U	4 E2G	4 E2G	5 E2G	5 E2G	5 E1U	5 E1U	1 A2G	4 B1U
	-0.2937	-0.2937	0.2478	0.2478	0.4803	0.5530	0.0239	0.0239	0.7023	0.7117	0.7117	0.0573	0.8573	0.8073	0.0073	1.0527	1.1282
1H1S	0.0	0.0	0.0	0.0	0.0	-0.5123	-0.0544	0.0	-0.4452	0.4401	0.0	-0.5812	0.0	-0.3101	0.0	0.0	-0.2930
2H1S	0.0	0.0	0.0	0.0	0.0	-0.5123	-0.3272	0.5007	0.4452	-0.2240	0.3881	0.2900	-0.5033	-0.1581	0.2730	0.0	0.2938
3H1S	0.0	0.0	0.0	0.0	0.0	-0.5123	0.3272	0.5007	-0.4452	-0.2240	-0.3880	0.2900	0.5033	0.1500	0.2737	0.0	-0.2938
4H1S	0.0	0.0	0.0	0.0	0.0	-0.5123	0.0544	0.0	0.4452	0.4481	0.0	-0.5011	0.0	0.3102	0.0	0.0	0.2938
5H1S	0.0	0.0	0.0	0.0	0.0	-0.5123	0.3272	-0.5007	-0.4452	-0.2240	0.3000	0.2900	-0.5033	0.1500	-0.2737	0.0	-0.2938
6H1S	0.0	0.0	0.0	0.0	0.0	-0.5123	-0.3272	-0.5067	0.4452	-0.2240	-0.3881	0.2900	0.5033	-0.1581	-0.2738	0.0	0.2930
1C1S	0.0	0.0	0.0	0.0	0.0	-0.0504	-0.0209	0.0	-0.1133	0.1544	0.0	0.0230	0.0	-0.0909	0.0	0.0	0.0509
2S	0.0	0.0	0.0	0.0	0.0	0.3411	0.1798	0.0	0.7182	-1.0300	0.0	-0.1071	0.0	0.7002	0.0	0.0	-0.4035
2PZ	0.5307	0.0	0.0021	0.0	-0.5284	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
X	0.0	0.0	0.0	0.0	0.0	0.3138	0.5507	0.0	0.0770	0.0502	0.0	0.0225	0.0	0.0857	0.0	0.0	0.0922
Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3402	0.0	0.0	-0.4273	0.0	-0.2211	0.0	-0.8419	-0.7800.	0.0
2C1S	0.0	0.0	0.0	0.0	0.0	-0.0504	-0.0134	0.0233	0.1133	-0.0772	0.1337	-0.0119	0.0200	-0.0454	0.0787	0.0	-0.0509
2S	0.0	0.0	0.0	0.0	0.0	0.3411	0.0899	-0.1557	-0.7182	0.5100	-0.0972	0.0930	-0.1021	0.3541	-0.0133	0.0	0.4035
2PZ	0.2053	-0.4590	-0.3310	0.5734	0.5284	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
X	0.0	0.0	0.0	0.0	0.0	0.1509	0.4003	-0.0903	-0.0305	0.3079	0.2008	-0.0390	0.4510	-0.0100	-0.4017	-0.0755	-0.3401
Y	0.0	0.0	0.0	0.0	0.0	-0.2718	-0.0903	0.5040	0.0007	0.2000	0.0091	0.4510	-0.5010	-0.4017	-0.1401	-0.3900	0.5995
3C1S	0.0	0.0	0.0	0.0	0.0	-0.0504	0.0134	0.0233	-0.1133	-0.0772	-0.1337	-0.0119	-0.0200	0.0454	0.0707	0.0	0.0509
2S	0.0	0.0	0.0	0.0	0.0	0.3411	-0.0899	-0.1557	0.7182	0.5180	0.8972	0.0930	0.1021	-0.3541	-0.0133	0.0	-0.4035
2PZ	-0.2053	-0.4590	-0.3310	-0.5734	-0.5204	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
X	0.0	0.0	0.0	0.0	0.0	-0.1509	0.4003	0.0903	-0.0385	-0.3079	0.2008	0.0390	0.4519	-0.0100	0.4017	-0.0755	-0.3401
Y	0.0	0.0	0.0	0.0	0.0	-0.2718	0.0903	0.5040	-0.0007	0.2000	-0.0091	0.4519	0.5010	0.4017	-0.1402	0.3900	-0.5995
4C1S	0.0	0.0	0.0	0.0	0.0	-0.0504	0.0209	0.0	0.1133	0.1544	0.0	0.0230	0.0	0.0909	0.0	0.0	-0.0009
2S	0.0	0.0	0.0	0.0	0.0	0.3411	-0.1790	0.0	-0.7182	-1.0300	0.0	-0.1872	0.0	-0.7002	0.0	0.0	0.4035
2PZ	-0.5307	0.0	0.0021	0.0	0.5204	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
X	0.0	0.0	0.0	0.0	0.0	-0.3130	0.5507	0.0	0.0770	-0.0502	0.0	-0.0225	0.0	0.0050	0.0	0.0	0.0922
Y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3402	0.0	0.0	0.4273	0.0	0.2210	0.0	-0.8419	0.7000	0.0
5C1S	0.0	0.0	0.0	0.0	0.0	-0.0504	0.0134	-0.0233	-0.1133	-0.0772	0.1337	-0.0119	0.0200	0.0454	-0.0707	0.0	0.0509
2S	0.0	0.0	0.0	0.0	0.0	0.3411	-0.0899	0.1557	0.7182	0.5100	-0.0972	0.0930	-0.1021	-0.3541	0.0133	0.0	-0.4035
2PZ	-0.2053	0.4590	-0.3310	0.5734	-0.5204	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
X	0.0	0.0	0.0	0.0	0.0	-0.1509	0.4003	-0.0903	-0.0305	-0.3079	-0.2000	0.0390	-0.4519	-0.0100	-0.4017	0.0755	-0.3401
Y	0.0	0.0	0.0	0.0	0.0	0.2710	-0.0903	0.5040	0.0007	-0.2000	-0.0091	-0.4519	0.5010	-0.4017	-0.1482	0.3900	0.5995
6C1S	0.0	0.0	0.0	0.0	0.0	-0.0504	-0.0134	-0.0233	0.1133	-0.0772	-0.1337	-0.0119	-0.0200	-0.0454	-0.0787	0.0	-0.0589
2S	0.0	0.0	0.0	0.0	0.0	0.3411	0.0899	0.1557	-0.7102	0.5180	0.0972	0.0936	0.1021	0.3541	0.0133	0.0	0.4035
2PZ	0.2053	0.4590	-0.3310	-0.5734	0.5204	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
X	0.0	0.0	0.0	0.0	0.0	0.1509	0.4003	0.0903	-0.0385	0.3079	-0.2008	-0.0398	-0.4510	-0.5100	0.4017	0.8755	-0.3481
Y	0.0	0.0	0.0	0.0	0.0	0.2710	0.0903	0.5040	-0.0007	-0.2008	0.0091	-0.4510	-0.5010	0.4017	-0.1481	-0.3900	-0.5995

IBM 7094, Model I, computer. Times for complete calculations using a given set of orbital exponents were 31 and 135 min for C_3H_6 and C_6H_6, respectively. The resulting eigenvalues and eigenvectors are given in Tables III and IV. One- and two-electron integrals over molecular orbitals were obtained using these coefficients and the integrals over basis orbitals.[5]

Energies

Cyclopropane and benzene provide two extreme examples of the interrelationship of molecular geometry and molecular energy. Unfortunately, current *ab initio* calculations are not sufficiently reliable to permit an unambiguous analysis of strain energy in cyclopropane or resonance energy in benzene. However, in this section we discuss the various components of the SCF energy obtained from the present wave function

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[5] Inquiries concerning the availability of copies of the one- and two-electron integrals over molecular orbitals (on magnetic tape) should be sent to Dr. R. M. Stevens.

Table V. Energies (au)

	C_3H_6[a]	C_3H_6[b]	C_3H_6[c]	C_3H_6[d]	C_3H_6[e]	C_6H_6[a]	C_6H_6[f]	C_6H_6[g]
Total energy	−116.8322	−117.0099	−116.9918	−116.9164	−116.7516	−230.2131	−230.463	−230.3745
Kinetic energy	116.9640		116.7766		114.9789	230.3367	230.266	228.5077
Nuclear attraction	−423.4722		−421.2331			−944.2800	−941.467	
$-E/T$	0.9989	0.9996	1.0018	1.0034	1.0154	0.9995	1.0009	1.0082

[a] Present calculations. [b] Reference 3f (Gaussian). [c] Reference 3e (Gaussian). [d] Reference 3a (Gaussian). [e] Reference 3g (minimum Slater). [f] Reference 3b (Gaussian). [g] Reference 3c (Gaussian).

and compare these results to those from other SCF calculations.[3] Calculated ionization potentials, atomization energies, and excitation energies are compared with experimental values.

Table V lists the various components of the SCF energy and compares the results obtained with our Slater-type basis to those from earlier calculations.[3] The speculation that the [3221] contracted Gaussian basis set of Schulman and Moskowitz[3b] would give energies slightly better than those from a minimum set of Slater-type orbitals is confirmed by these results. An earlier paper[6] discussed the various choices of atomic reference states in the calculations of atomization energies from minimum basis set molecular SCF energies. Table VI lists atomization energies calculated with various reference states and compares these results with the experimental values. The fortuitous cancellation of energies observed in the boron hydride atomization calculation, which employed constrained atom reference states,[6] is found to be less reliable in molecules with multiple bonds such as benzene.

Table VI. Atomization Energies (au)

	C_3H_6	C_6H_6
Best-atom reference states[a]	0.965	1.479
Constrained-atom reference states[b]	1.224	1.879
Experimental	1.295[c]	2.099[c]

[a] Atomic calculations of E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38,** 2686 (1963), used as reference states. [b] Reference state taken from atomic calculation with molecular exponents; see ref 7. [c] H. A. Skinner and G. Pilcher, *Quart. Rev., Chem. Soc.*, **17,** 264 (1963).

The ionization potentials and orbital energies in cyclopropane and benzene have been studied by photoelectron and Rydberg spectroscopy. Table VII compares these experimental values to the Koopmans' ionization potentials calculated from SCF orbital energies.[7] There is good agreement between the calculated and experimental value for cyclopropane. The relative ordering of the σ and π levels of benzene has been considered in two recent analyses of photoelectron and Rydberg spectra and other experimental data.[8] In agreement with other *ab initio* calculations[3b,c] and the experimental analysis of Lindholm and Jonsson[8a] this calculation finds only one σ level ($3e_{2g}$) between the two occupied π levels. These results disagree with semiempirical calculations[9] and other recent interpretations of experimental data[8b] which indicate that two or more σ orbitals lie between the two occupied π levels. Table VII indicates reasonable agreement between the results of this calculation and the higher ionization potential assignments of Lindholm and Jonsson.[8a]

Table VII. Ionization Potentials (eV)

	Calcd	Exptl	
	C_3H_6		
	10.52	10.09[a]	
	C_6H_6		
$^1e_{1g}(\pi)$	7.99	9.3[b]	9.24[c]
$^3e_{2g}$	12.03	11.4	10.35
$^1a_{2u}(\pi)$	12.72	12.1	11.50
$^3e_{1u}$	14.77	13.8	
$^1b_{2u}$	15.30	14.7	10.85
$^2b_{1u}$	16.43	15.4	
$^3a_{1g}$	18.22	16.9	
$^2e_{2g}$	21.15	19.2	

[a] K. Wantanabe, *J. Chem. Phys.*, **26,** 543 (1957). [b] Values in this column from ref 8a. [c] Values in this column from ref 8b.

The interpretation of the molecular spectrum of benzene provided the impetus for many of the early molecular orbital calculations.[10] The presence of many degenerate and nearly degenerate orbitals suggests that only a complete configuration-interaction (CI) calculation will provide a satisfactory interpretation of the experimental results. Table VIII lists the excitation energies for the various electronic states arising from the $1e_{1g} \rightarrow 1e_{2u}$ ($\pi \rightarrow \pi^*$) transition. These single-configuration excitation energies are compared to the analogous values from the Gaussian lobe calculations of Buenker, Whitten, and Petke.[3c] These authors found the same (incorrect) ordering of states in their

Table VIII. Transition Energies for $^1e_{1g} \rightarrow {}^1e_{2u}$ ($\pi \rightarrow \pi^*$) Excitations in Benzene

	Calcd[a]		
State	This work	BWP[c]	Exptl[b]
$^3B_{1u}$	4.55	4.54	3.66
$^3E_{1u}$	5.94	5.73	4.59
$^3B_{2u}$	7.33	6.92	5.76
$^1B_{2u}$	7.54	7.15	4.89
$^1B_{1u}$	9.07	8.38	6.14
$^1E_{1u}$	11.71	10.93	6.76

[a] Gilman and De Heer,[3d] using the alternate molecular orbital method, calculate a $^3B_{1u}$ transition of 3.77 eV. Their results, and the CI treatment of Buenker, Whitten, and Petke,[3c] are to be compared with CI results obtained from our wave function.[11] [b] D. R. Kearns, *J. Chem. Phys.*, **37,** 1608 (1962). [c] Reference 3c.

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(6) E. Switkes, I. R. Epstein, J. A. Tossell, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **92,** 3837 (1970).

(7) (a) T. Koopmans, *Physica*, **1,** 105 (1933); (b) M. D. Newton, *J. Chem. Phys.*, **48,** 2825 (1968).

(8) (a) E. Lindholm and B.-Ö. Jonsson, *Chem. Phys. Lett.*, **1,** 501 (1967); (b) J. Momigny and J. C. Lorquet, *ibid.*, **1,** 505 (1967).

(9) (a) R. Hoffmann, *J. Chem. Phys.*, **39,** 1397 (1963); (b) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88,** 2367 (1966); (c) M. J. S. Dewar and G. Klopman, *ibid.*, **89,** 3089 (1967).

(10) R. G. Parr, D. P. Craig, and I. G. Ross, *J. Chem. Phys.*, **18,** 1561 (1950), and references therein.

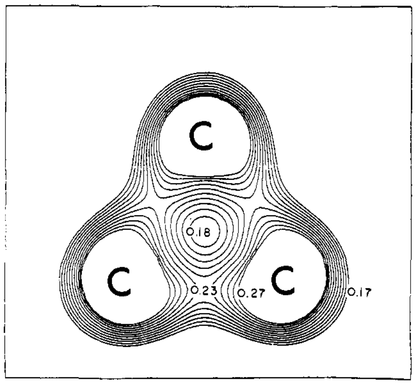

Figure 1. Total electron density in three-carbon plane of cyclopropane. Contours spaced at intervals of 0.01 electron/au^3.

single-configuration results. On the basis of an extensive CI treatment, Buenker, *et al.*,[3] predict the observed order for the $^1B_{2u}$ transition but raise questions about the experimental assignment of several higher states. The Slater-orbital wave function given here will provide an appropriate starting point for CI calculations which hopefully will clarify these assignments.[11]

Population Analysis and Bonding

Cyclopropane. The nature of the electron distribution in the C–C bonding region of cyclopropane has been a subject of great interest. Tables IX and X list overlap and orbital populations,[12] net atomic charges,[12] and bond moments.[13] Comparison of the overlap population in the "strained" C–C bonds of cyclopropane (0.609 electron) with that in the "normal" C–C single bond in ethane[2b] (0.759 electron) indicates a significant reduction in bonding. A second indication of anisotropy in the C–C bond is found in the nonzero bond moment (1.0 D), which has a direction perpendicular to the C–C direction and sense indicating greater electron density exterior to the ring.

Table IX. Overlap Populations and Bond Moments

Bond	Overlap population[a]	Bond moment, D
	C_3H_6	
1C–1H	0.799	1.14
1C–2C	0.609	1.00
	C_6H_6	
1C–1H	0.794 (0.833)	1.13
1C–2C	1.035 (0.977)	0.00
1C–3C	−0.058 (−0.250)	0.01
1C–4C	−0.026 (−0.061)	0.00

[a] Values in parentheses are from Gaussian calculations of ref 3b.

Table X. Orbital Populations and Net Atomic Charges

	C_3H_6	C_6H_6
	Populations	
H 1s	0.942	0.935
C 1s	1.995	1.995
C 2s	1.126	1.107
C $2p_z$	1.017	1.000
C $2p_x$	0.886	0.996
C $2p_y$	1.091	0.967
	Charges	
H	0.058	0.065 (0.23)[a]
C	−0.115	−0.065 (−0.23)

[a] Values in parentheses are from Gaussian calculations of ref 3b.

Several measures may be used to determine the degree of "bent" bonding in the cyclopropane ring. An objective procedure which isolates a C–C bond from the total electron density has been applied to our cyclopropane wave function.[14] The hybrids involved in the localized C–C bond form an angle of 28° with the internuclear direction. Alternatively, the relative p_x and p_y orbital populations listed in Table X indicate an angle of 21°. These estimates are in accord both with earlier calculations,[15] which give a bonding angle of 22°, and with an experimentally determined angle of 20 ± 10° obtained from X-ray diffraction data.[16]

Since the partitioning of the total electron density and dipole moment according to Mulliken[12] and Ruedenberg[13] are not invariant to transformations *within* the basis set, comparison of population indices from calculations employing different basis sets must be viewed with caution (*e.g.*, the comparison of Slater and Gaussian calculations in Tables IX and X). Fortunately, the total electron density at a point is invariant to such transformations. Figure 1 plots the calculated electron density in the C–C–C plane of cyclopropane.[17] As was previously noted,[14] the large calculated and experimental bonding angles belie the absence of significant "bending" of the total C–C electron density. In fact, the ridge of maximum electron density of the C–C bond in Figure 1 makes an angle of 8.5° with the C–C direction. This measure is consistent with a similar angle of 7.5° found in a semiempirical calculation.[18]

The difference between the molecular electron density and that of the constituent atoms provides a useful picture of bonding. Figures 2 and 3 show the difference of the cyclopropane electron density calculated from our wave function and that obtained from the sum of spherical-atom electron densities. SCF wave functions employing the molecular exponents were used to determine the carbon and hydrogen atomic densities. In Figure 2 the carbon atom reference state is s^2p^2, ^3P, while in Figure 3 the reference state is sp^3, ^3P. Both maps clearly show the accumulation of charge in the region of the C–C bond. Specifically, the peak difference density in the region of the C–C bond corresponds to an increase of 0.295 electron/Å^3 for Figure 2 and 0.308 electron/Å^3 for Figure 3. The similarity between Figures 2 and 3 is due largely to the near equality of the carbon 2s and 2p exponents in our optimized basis set.

Comparison of our maps with analogous plots which utilize molecular densities determined experimentally from X-ray studies on cyclopropane derivatives[16,19]

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(11) A CI study with the present wave function is being conducted by Professor K. Morokuma.

(12) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(13) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).

(14) M. D. Newton, E. Switkes, and W. N. Lipscomb, *J. Chem. Phys.*, **53**, 2645 (1970).

(15) (a) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949); (b) C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 3161 (1963).

(16) C. J. Fritchie, *Acta Crystallogr.*, **20**, 27 (1966).

(17) This map may be compared to the analogous plot given by Buenker and Peyerimhoff; see ref 3a.

(18) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).

(19) (a) A. Hartman and F. L. Hirshfeld, *Acta Crystallogr.*, **20**, 81 (1966); (b) A. Hartman, Thesis, The Weizmann Institute of Science, Rehovot, Israel. Address inquiries to Professor F. L. Hirshfeld.

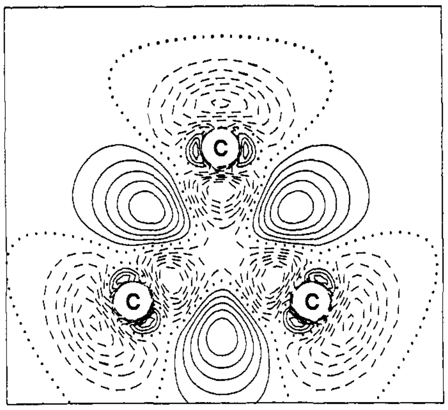

Figure 2. Difference density (molecular electron density minus sum of spherical atom densities) in cyclopropane three-carbon plane. Solid lines indicate positive density, dotted lines zero density, dashed lines negative density. The contour interval is 0.05 electron/Å^3. The carbon atom reference state is s^2p^2, ^3P.

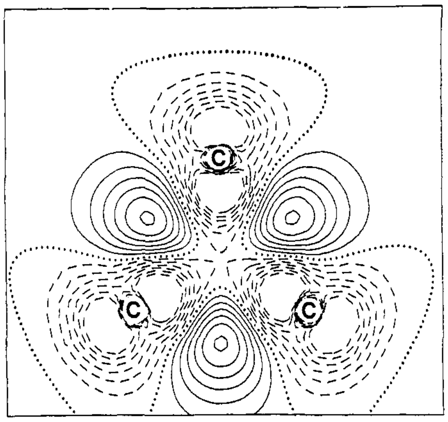

Figure 3. Difference density analogous to Figure 2. The carbon atom reference state is sp^3, ^3P.

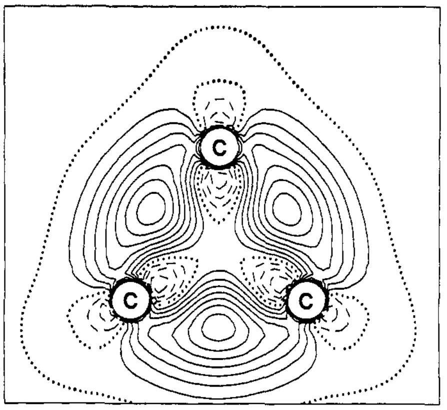

Figure 4. Difference density analogous to Figure 2. The carbon atom wave function is a numerical Hartree–Fock s^2p^2, ^3P. Peak difference density in C–C bond region is 0.380 electron/Å^3.

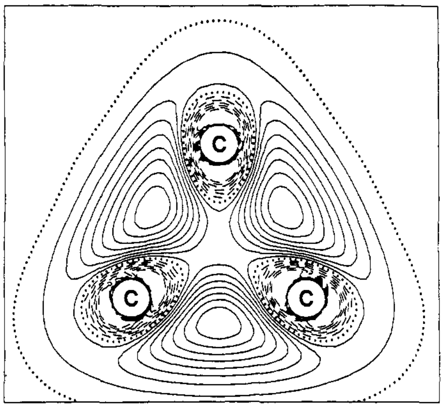

Figure 5. Difference density analogous to Figure 3. The carbon atom wave function is a numerical Hartree–Fock sp^3, ^3P. Peak difference density in the C–C bond region is 0.445 electron/Å^3.

indicate qualitatively good agreement. However, the effects of thermal vibrations, series termination, and least-squares refinements on the experimental results, and the inadequacies of a minimum basis set on the theoretical calculations all tend to diminish quantitative agreement between experimental and theoretical maps. Thus, for example, experimental difference density maps obtained from low-temperature (~80°K) X-ray work show strikingly better agreement with our calculated maps.[19b]

As previously discussed,[6] the use of optimized molecular exponents for the atomic reference states does not allow for the effects of orbital contraction on molecular binding.[13] However, use of numerical Hartree–Fock wave functions[20] (Figures 4 and 5) for the carbon atom reference states actually worsens the quantitative agreement between theory and experiment. Although the results of Hartman and Hirshfeld[19] depend on scattering factors calculated from a numerical Hartree–Fock wave function,[21] subtraction of numerical Hartree–Fock carbon densities from our minimum basis set molecular function apparently produces an unbalanced map, in which the shortcomings of the minimum basis set are uncompensated. In Figures 2 and 3 these deficiencies hopefully tend to cancel.

The greater flexibility of the Hartree–Fock atomic orbitals *vis-à-vis* our minimum basis set orbitals is reflected in the significant discrepancy between Figures 4 and 5 as compared to the relatively small difference between Figures 2 and 3. However, both comparisons show that subtraction of the atomic sp^3, ^3P state gives a greater increase of charge in the C–C bonding region than does subtraction of an s^2p^2, ^3P state. In general then, the choice of atomic reference state may be significant, and comparisons between theoretical and experimental difference densities should consider this fact. Consequently, we strongly recommend that experimentalists and theoreticians make available *both* the wave functions and the scattering curves from which their difference densities are obtained. Accordingly, we include in Tables XI and XII the scattering factors and relevant expansion coefficients for the carbon atom wave function used in our difference-density maps.[22]

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(20) The numerical Hartree–Fock wave functions for carbon are reported by A. Jucys: for s^2p^2, *Proc. Roy. Soc., Ser. A*, **173**, 64 (1939); and, for sp^3, *J. Phys. (USSR)*, **11**, 49 (1947). The latter was kindly supplied to us by Dr. Jucys.

(21) The scattering factors used by Hartman and Hirshfeld are reported by J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Crystallogr.*, **8**, 478 (1955). An apparently identical calculation by V. R. Allman [*ibid.*, **22**, 432 (1967)] gives scattering factors which differ by as much as 0.08. These discrepancies remain unresolved.

(22) All scattering factors were calculated on an IBM 360-65 computer. The scattering factors for the Slater basis set were determined by

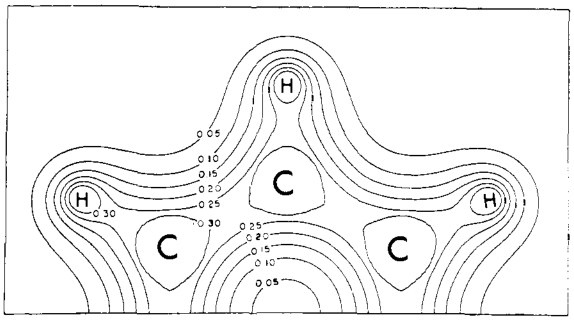

Figure 6. Total electron density in molecular plane of benzene (upper half of molecule).

Benzene. Many of the unique chemical and physical properties of benzene have been attributed to the interaction of the six π electrons. A comparison of calculated C–C overlap populations in the series ethane,[2b] *trans*-butadiene[23] (interior C–C bond), and ethylene[2a] (0.759, 0.840. 1.219, respectively) with benzene (1.035) indicates that the benzene C–C bonding density is, as expected, intermediate between that of a single and a double bond and that benzene displays significantly greater delocalization than is found across the "single bond" in *trans*-butadiene. The negative 1C–4C overlap population gives no indication of net bonding across the ring, although the importance of Dewar structures cannot be eliminated without a careful study which permits a multiplicity of configurations and which considers the magnitudes of normal negative-overlap populations arising from nonbonded repulsions.[24] Figure 6 displays the total molecular electron density in the upper half-plane of the benzene molecule.

Table XI. Atomic Scattering Factors for Carbon ^3P Wave Functions

$\sin(\theta)/\lambda$, radians/Å	s^2p^2 Minimum Slater	s^2p^2 Numerical HF	sp^3 Minimum Slater	sp^3 Numerical HF
0.05	5.811	5.75 ± 0.01	5.812	5.73 ± 0.01
0.10	5.300	5.12 ± 0.01	5.303	5.05 ± 0.01
0.15	4.599	4.32 ± 0.02	4.605	4.24 ± 0.02
0.20	3.861	3.56 ± 0.02	3.871	3.50 ± 0.02
0.25	3.199	2.94 ± 0.02	3.212	2.91 ± 0.02
0.30	2.668	2.48 ± 0.02	2.684	2.48 ± 0.02
0.35	2.276	2.16 ± 0.02	2.293	2.17 ± 0.02
0.40	2.002	1.93 ± 0.02	2.018	1.95 ± 0.02
0.50	1.689	1.67 ± 0.01	1.698	1.69 ± 0.01
0.60	1.532	1.525 ± 0.01	1.532	1.54 ± 0.01
0.70	1.425	1.42 ± 0.01	1.417	1.42 ± 0.01
0.80	1.327	1.31 ± 0.01	1.312	1.30 ± 0.01
0.90	1.228	1.21 ± 0.01	1.208	1.20 ± 0.01
1.00	1.126	1.107 ± 0.006	1.104	1.089 ± 0.006
1.10	1.026	1.006 ± 0.005	1.002	0.987 ± 0.005
1.20	0.928	0.910 ± 0.004	0.904	0.891 ± 0.004
1.30	0.836	0.818 ± 0.002	0.813	0.800 ± 0.002

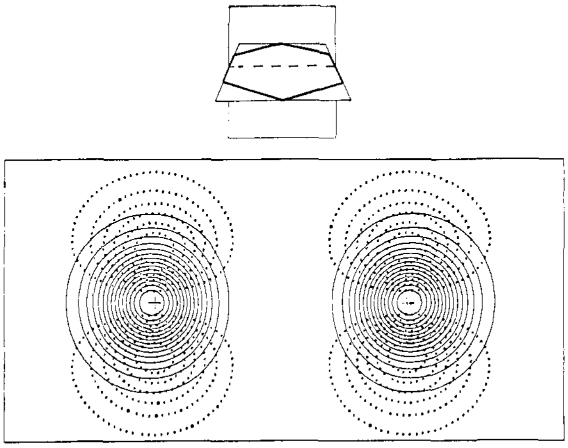

Figure 7. Superposition of the $3e_{2g}$ (σ) and $1e_{1g}$ (π) molecular orbitals in benzene. Plane perpendicular to the molecular plane of benzene and bisecting opposite C–C bonds. Contours start at 0.004 electron/au^3. Contour interval 0.004 electron/au^3.

Table XII. Expansion Coefficients for Minimum Basis Set Carbon Wave Functions

Basis orbital	Exponent	1s	2s	2p
		s^2p^2, ^3P		
1s	5.68	0.99634	−0.2689	0.0
2s	1.74	0.01441	1.03191	0.0
2p	1.7118	0.0	0.0	1.0
		sp^3, ^3P		
1s	5.68	0.99605	−0.27007	0.0
2s	1.74	0.01554	1.03189	0.0
2p	1.7118	0.0	0.0	1.0

The concept of $\sigma-\pi$ separation in molecular calculations[10,25] was originally based on an assumption of the independence of the π electrons above and below the plane of the molecule and the σ electrons localized near the molecular plane. Earlier all-electron calculations suggested strong interpenetration of the σ- and π-electron densities.[9b] Figure 7 is a superposition of the electron densities in the highest occupied σ ($3e_{2g}$) and highest occupied π ($1e_{1g}$) molecular orbitals in benzene. The plane of the figure is perpendicular to the molecular plane and bisects opposite C–C bonds. The degree of penetration of these electron distributions indicates a significant interaction between the σ and π

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exact formulas. For the numerical Hartree–Fock wave functions, the integrals

$$\int_0^{r_1} P_K^2(r) \sin(\mu r)/\mu r \, dr$$

where $\mu = 4\pi(\sin\theta)/\lambda$, were uniformly calculated as follows: (i) to the same upper limit, $r_1 = 13a_H$, where a_H is the Bohr radius; (ii) in the same steps, $r/a_H = 0\ (0.005),\ 0.3\ (0.05),\ 13.0$ (for the latter purpose the data from the literature were interpolated linearly to the required intervals; integrations were performed using Simpson's rule).

The integrations were checked as follows: (i) by the normalizing integral

$$\int_0^{r_1} P_K^2(r) dr$$

(ii) by interpolating the total density, and by interpolating the value of each MO; (iii) in the case of the s^2p^2, ^3P function, by comparison with scattering factors for the analogous Slater basis set: E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.*, **127**, 1618 (1962). A check of point densities showed the Slater set values to agree with the numerical Hartree–Fock results to at least 0.14% (the numerical Hartree–Fock values are reported to only three significant figures) for $0 < r < 3.0$ au, and to at least 0.00001 electron/au^3 for larger values of r.

(23) E. Switkes, unpublished.

(24) (a) M. D. Newton and C. A. Coulson, *Mol. Phys.*, **15**, 305 (1968); (b) C. A. Coulson, *ibid.*, **15**, 317 (1968).

(25) (a) L. Pauling, *J. Chem. Phys.*, 4, 673 (1936); (b) T. Itoh, K. Ohno, and H. Yoshizumi, *J. Phys. Soc. Jap.*, **10**, 103 (1955); (c) J. Baudet, J. Guy, and J. Tillieu, *J. Phys. Radium*, **21**, 600 (1960); (d) G. G. Hall and A. Hardison, *Proc. Roy. Soc., Ser. A*, **268**, 328 (1962); (e) A. T. Amos and H. G. Roberts, *J. Chem. Phys.*, 50, 2375 (1969).

electrons. Also noteworthy is the shift of the $3e_{2g}$ density toward the outer side of the benzene ring. However, the small bond moments (compare to C_3H_6) listed in Table IX indicate that the total electron density in each C–C bond is almost isotropic.

Magnetic Properties of Benzene

Calculation of the anisotropy in the magnetic susceptibility tensor for benzene has been the subject of much theoretical work.[25] Past experience[26] has shown that a thorough treatment of this problem by the method of coupled Hartree–Fock theory would require a basis set roughly three times our minimal Slater set. Presently such calculations are impractical. Thus, for example, recent calculations[25e,d] have concentrated primarily on the contribution of the π electrons, taking the contributions of the localized σ electrons from empirical values.

The magnetic susceptibility is expressed as the sum of two terms of opposite sign, a negative, or diamagnetic term, and a positive, or paramagnetic term. Using our minimum Slater basis set wave function, we have calculated the diamagnetic term with the gauge origin at the center of electronic charge. Use of this particular gauge origin facilitates comparison with the experimental results of Shoemaker and Flygare[27] and provides for hopefully minimal error, since the diamagnetic term, which is proportional to the expectation value of the second-order Hamiltonian, has a minimum in absolute value for this choice of gauge origin.[28] Our previous experience[29] has indicated that an optimized minimum Slater set is adequate to describe this diamagnetic contribution. The results of our calculation are shown in Table XIII. The agreement with experiment is excellent.

Table XIII. Components of the χ^d Tensor of Benzene with Gauge Origin at Center of Electronic Charge

	Present calculations	Exptl[a]
	χ_{zz}^d, ppm	
σ electrons	−453.82	
π electrons	−55.46	
Total	−509.28	−508 ± 20
	$\chi_{xx}^d = \chi_{yy}^d$, ppm	
σ electrons	−246.23	
π electrons	−39.76	
Total	−285.99	−286 ± 10

[a] See ref 27.

It is noteworthy that the π-electron contribution to χ_{zz}^d differs by only 4.2 ppm from the experimental anisotropy of 59.7 ppm.[30] The much earlier work of Pauling,[25a] based on the concept of σ–π separability and a cylindrically symmetric potential for the π electrons, assumed these two quantities to be equal. However, the significant interpenetration of σ and π electron densities indicated in Figure 7 seriously questions the former of these assumptions. Thus a fortuitous cancellation of terms is responsible in part for the apparent accuracy of Pauling's original calculation. From the calculated anisotropy $-509 + 286 = -223$ ppm of the diamagnetic term (Table VIII) and the experimental total ansiotropy of 60 ppm we suggest that the anisotropy in the paramagnetic terms is $\chi_{zz}^p - \chi_{xx}^p = \chi_{\perp}^p - \chi_{\parallel}^p = 163$ ppm.

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