

Isolation and Characterization of a Fourth Fullerene C78 Isomer

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Substantial amount of experimental and theoretical efforts has been devoted to the study of fullerenes. The isolation of C60 and C70 by chromatography has shown the simultaneous presence of so-called higher fullerenes, larger even-numbered carbon cage structures than C70 such as C76, C78, C82 and C84 [1-3]. These fullerenes are considered to obey isolated pentagon rule (IPR) [10]. Among the higher fullerenes, C78 has been the subject of many experimental [4-9] and theoretical investigations [10-20]. Fowler and Manolopoulos found that there are five possible structures for C78 satisfying the IPR rule [10]. The five structural isomers include two with D3h symmetry, one with D3 symmetry, and the other two with C2v symmetry [10]. Following the definition described in ref. 10, these isomers will be reported as the D3h(1), D3h (2), D3(3), C2v(4), and C2v(5) isomers.

Experimental analysis by ¹³C NMR spectroscopy has been very useful in clarifying the structural properties of actual C78 molecules [4-7]. Diederich et al. reported isolation of two forms of the C78 isomers, D3(3) and C2v(4) [4a]. They estimated the D3(3): C2v(4) ratio to be 1:5. Later Kikuchi et al. [5] identified the presence of the two distinct C2v forms of C78, in that the C2v(5) isomer is the most abundant, along with the D3 (3) isomer in a 2:2:5 ratio. The presence of the same kind of three isomers as found by Kikuchi, D3(3): C2v(4): C2v(5), was also identified in the ratio 3:5:2 by Taylor et al. [6,7]. The isomer ratio for C78 reported so far differs from each other, which was once explained by considering the difference of soot-generation conditions [8].

On the other hand, there was little experimental evidence for the presence of for C78 isomers with D3h symmetry. Recently ³He NMR spectroscopy of higher fullerene mixtures containing mostly C78 has revealed the possibility that there are at least five C78 isomers [9], suggesting the presence of D3h-symmetry isomers. But due to the incomplete separation of the sample and possible presence of C80, C82, and C84 isomers, the existence of C78 with D3h symmetry is not evident.

These experimental studies of C78 have stimulated much effort to predict and estimate the stability, structure, and other properties of these C78 fullerene molecules theoretically [4a, 10-20]. Using Huckel MO theory, Fowler et al. predicted that the D3h(1) isomer with a large HOMO-LUMO gap would be the most stable [10]. Liu et al. [11a] and Taylor [11b] also predicted that the D3h(1) isomer is the most stable. However D3h(1) isomer was predicted to be the least stable form at MM3 [4a, 14], empirical tight-binding model [12], semi-empirical MNDO model [13], local-density-functional technique [15], and ab initio calculation level [13-15,20]. This means the gsteric factor

may also be important for the evaluation of fullerene stability [16]. While the total energy ordering in the resultant four isomers, D3h(2), D3(3), C2v(4), and C2v(5) varies with the level of theory, they are within a few kcal/mol [12-16,20]. Sometimes the D3h(2) isomer is calculated to be more stable than the D3(3) isomer [12,13,15]. From their thermodynamic point of view, the D3h(2) isomer should be produced along with the D3(3), C2v(4), and C2v(5) isomers. On the contrary, Saito et al. [19] predicted that the D3h(1) may also be an extractable isomer from the similarity of the other extractable fullerenes.

A forth isomer of C78 has been isolated for the first time with an efficient high performance liquid chromatography method. In this presentation, we describe the first isolation and structural confirmation of this isomer. ¹³C NMR spectroscopy and electrochemical properties for the isomer revealed that it is D3h(2)-C78.

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