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A re-examination of the crystal and molecular structure of azulene as is present in LADWEW = tris(1,2,4,5-tetrafluoro-3,6-diiodobenzene) bis(azulene), 2($C_{10}H_8$), 3($C_6F_4I_2$) - a conglomerate in *P*1

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RESEARCH ARTICLE

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ABSTRACT

In need of information on the precise structural data of the monomer of azulene, we were long frustrated by our inability to characterize it thus because the known specimens always contained its extremely stable head-to-tail dimer. Recently, a claim was made of having prepared such a monomeric species in the case of (tris(1,2,4,5-tetrafluoro-3,6-diiodobenzene)bis(azulene), whose REFCODE = LADWEW), which the authors used to "demonstrate how a highly robust C-I···π motif permits the systematic exchange of original co-crystal components with azobenzene and azulene, resulting in optically interesting dichroic or pleochroic materials." We demonstrate that the structural data used in the theoretical treatment of the title compound were derived from an improper crystallographic analysis. The *hkl* values provided in the original report were used to obtain the correct structural solution in *P*1, (Z' = 1) as opposed to the original centrosymmetric *P*-1, (Z' = 0.5) interpretation. These new data have been deposited with the CCDC #2403565.

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1. Introduction

We have been interested in the properties of azulene for some time, the first example being a paper [1] on cyclic voltammetry, electron spin resonance, and quantum mechanical properties of this molecule; that paper was plagued by the long-persistent problem that the crystals of pure azulene consist of seemingly inseparable dimers; all attempts failed to separate them into the convenient pair of monomers needed to produce the accurate bond lengths and angles necessary to complete the theoretical analyses included in the quoted [1] publication.

Recently, our interest in the subject was revived and we have completed a study of anion radicals of derivatives of azulenes, such as guaiazulene, that allows the facile separation of the dimer [2]; and, in the process of re-examining the existing literature, we encountered a very interesting claim [3] that crystals of the title compound contain monomeric azulene that had been separated from its common dimeric form by a donor-acceptor interaction with 1,2,4,5-tetrafluoro-3,6-diiodobenzene. Thus, we decided to use those results as comparison standards in our work, since the crystallographic markers published [3] gave impressively: R = 2.51% at T = 150 K.

To our great surprise, we discovered that the molecular description of that structure, using the CIF file provided by the CSD [4] compilation, was disturbing because a plot of the molecular species present in the unit cell revealed some questionable crystallographic information, to wit: [In the following sections, the Discussion and Conclusions are based on the hkl file of the LADWEW [3] structure, which was reprocessed by us in space group *P*1].

(1) The two azulene molecules in the asymmetric unit of LADWEW [3] are united by π-π interactions in a cluster of four components that is shown in Figure 1. In this figure, the π-π interactions are all 5.962 Å (exactly the *a* cell dimension = 5.9617(2) Å) (shown in the vertical direction below), most probably due to packing considerations; however, in the horizontal direction, the π-π interactive distances range from 4.01(2) to 4.80(3) Å, with an average value of 4.45(3) Å.

(2) The refinement using the authors' *hkl* data [3] in the correct space group *P*1 yields a Flack value x of 0.41(3); this is far enough removed from the value of 0.50 expected from a centrosymmetric structure because **x** should be either 0.0 or 0.50 exactly. In fact, since **x** is 0.41, it shows that this crystal is from a Sohncke space group in which a significant fraction of the largest scattering atoms (the six iodine atoms) is close to an

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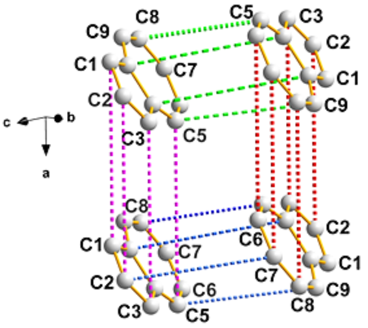

Figure 1. The cluster of four azulenes present in the lattice with π-π contacts listed above [3].

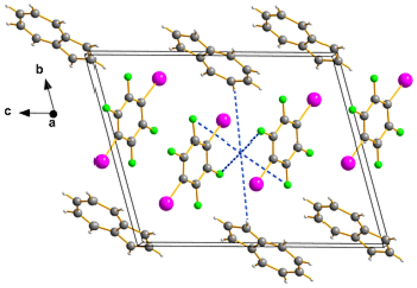

Figure 2. A partial packing diagram of the molecule in space group *P*1 (this work).

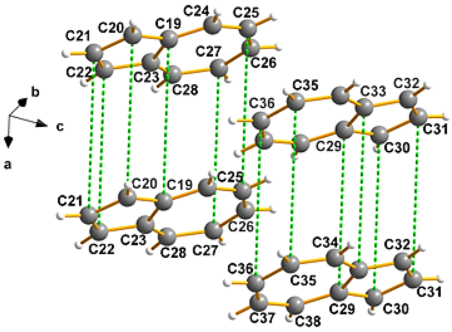

Figure 3. The two molecules of azulene in the asymmetric unit form homogenous pairs of (mol1)-(mol1) and (mol2)-(mol2), both aligned exactly along the *a*-direction in *P*1.

imperfect center of symmetry typical of one of its proper super groups.

We have recently published a paper [5] in which we proved that observations (1) and (2) above are characteristic of crystals in which anomalous molecular aggregates and Flack **x** values are typical of structures belonging to a Sohncke space group, but were refined in a higher-symmetry one. In the case of Sohail *et al.* [5], there was a Co atom and three I atoms clustered in a pseudo-inversion center, close to a true one of the higher space group choice. The interested readers are directed to that lengthy paper whose X-ray conclusions were backed by Second Harmonic measurements [5].

2. Experimental

In view of the above observations, we decided to obtain the data deposited by the authors with CSD [4], and independently solve the structure in space group *P*1, which is the proper subgroup of *P*-1. In space group *P*1, the origin is totally arbitrary and must be set and fixed for the refinement to converge. Therefore, in order to have a common point with the results of the centrosymmetric treatment of the data from the previous report of Vainauskas *et al.* [3], we set the coordinates of our iodine (1) to be the same as those in Vainauskas *et al.* [3] and proceeded as follows: in the 1st difference electron density map, we found 5 more large peaks which were ascribed to be the 5 other iodine atoms required in *P*1. In subsequent difference maps, ALL of the remaining atoms of the tetrafluorodiiodophenyl groups were found. Then, in subsequent difference electron density maps, the azulene carbon atoms appeared. which were refined, whereupon the H atoms for the azulenes appeared in further difference electron-density maps. The non-hydrogen atoms were refined anisotropically and the refinement converged to R of 2.64%, with a Flack **x** = 0.41(3), as expected, since the data are those of an imperfect centro-symmetric space group. The data have been deposited as CCDC # 2403565. Our figures were generated using the graphic program DIAMOND [6] and some of the manipulations and calculations were done using MERCURY [7].

3. Results and Discussion

The unit cell in *P*1 is shown in Figure 2, as a projection down the *a* axis. The blue dotted lines in Figure 2 converge to a pseudo-inversion center of 0.4980, 0.5017, 0.5006, remarkably close to an ideal ½, ½, ½ value typical of a centrosymmetric *P*-1 case. Note that in *P*1 (this work), the azulene dimer also appears as separate monomeric entities, as correctly claimed in the original [3] report.

Concerning the presence of π-π contacts, Figure 3 graphically summarizes the results one obtains from the *P*1 refinement. The distances between the atomic pairs (see Figure 3) are 5.962 Å, which, within the experimental error, corresponds to the value of the *a*-cell dimension, 5.9617(2) Å; this is longer than the value recommended for strong bonds (approximately 4.0 Å) [8]. However, given Avogadro's number, it amounts to a considerable amount of energy. Therefore, the crystalline packing forces largely drive the contacts shown in Figure 3, and the azulene molecules are, indeed, isolated from one another.

4. Conclusions

Our results are as follows: (i) Vainauskas *et al.* [3] did break the azulene dimer into well-isolated monomers, which is indeed a very important result, for the reasons stated above. (ii) The resulting species: tris(1,2,4,5-tetrafluoro-3,6-diiodobenzene) bis(azulene), $2(C_{10}H_8)$, $3(C_6F_4I_2)$, appearing in CSD [4] as LADWEW [3], is a case of conglomerate crystallization with Z' = 1.0, which crystallizes in space group *P*1. (iii) It is beginning to be observed more and more frequently that conclusion (b) is a common occurrence in crystallography; interested readers are directed to Sohail *et al.* [5] for an extensive discussion of the topic, giving additional examples in the CSD [4]. (iv) Our refinement in *P*1, yielding the atomic positions used to generate all our figures, gives a final R = 2.64% and a Flack **x** of 0.41(3); this R-factor is fully as good as that originally given by Vainauskas, *et al*. [3], and the Flack **x** is that of a true Sohncke space group.

Supporting information

CCDC-2403565 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

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Competing interests: The authors have declared that no competing financial or personal interests exist.
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CRediT authorship contribution statement

Conceptualization: Ivan Bernal, Roger A. Lalancette; Methodology: Ivan Bernal, Roger A. Lalancette; Software: Ivan Bernal, Roger A. Lalancette; Validation: Ivan Bernal, Roger A. Lalancette; Formal Analysis: Ivan Bernal, Roger A. Lalancette; Investigation: Ivan Bernal, Roger A. Lalancette; Resources: Ivan Bernal, Roger A. Lalancette; Data Curation: Ivan Bernal, Roger A. Lalancette; Writing - Original Draft: Ivan Bernal, Roger A. Lalancette; Writing - Review and Editing: Ivan Bernal, Roger A. Lalancette; Visualization: Ivan Bernal, Roger A. Lalancette; Supervision: Ivan Bernal, Roger A. Lalancette; Project Administration: Ivan Bernal, Roger A. Lalancette.

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